Reactivity Studies of Low-valent Germanium and Tin N-Functionalized Amides and Alkyls

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Abstract

The work presented in this thesis mainly focuses on three areas: (i) synthesis and characterization of low-valent Group 14 organometallic complexes using the aza-allyl ligand [$\bar{N}(SiMe_3)C(Ph)C(SiMe_3)C_5H_4N$-2] ($\bar{R}^1$); (ii) reactivities of these low-valent Group 14 organometallic complexes and (iii) the chemistry of halogenated compound containing N-functionalized alkyl compound [$Sn(R^2)_2$] (**27**).

Chapter 1 gives an introduction on the general aspects of Group 14 organometallic chemistry and deals with the synthesis and characterization of germanium(II) alkenyl amide [$Ge(R^1)(R^{1'})$] (**29**), tin(II) amide [$Sn(R^1)_2$] (**30**) and tin(IV) amide dichloride [$Sn(R^1)_2Cl_2$] (**31**). Complexes **29** to **31** have been characterized by X-ray structure analysis. Compounds **29** and **30** are shown to be monomeric in nature.

Chapter 2 begins with a brief introduction on the synthesis and reactivities of Group 14 chalcogenone. The reactions of low-valent Group 14 complexes **29** and **30** with elemental sulfur and selenium have been investigated. The corresponding metal chalcogenone complexes [$(R^1)(R^{1'})M=E$] [M = Ge, E = S (**59**), Se (**60**); M = Sn, Se (**62**), [$(R^1)_2Sn=S$] (**61**)], have been isolated and characterized structurally.

Chapter 3 describes the reacitvities of low-valent Group 14 organometrallic compounds with Group 11 metal derivatives. Tin(II) compound [$(R^2)_2Sn$] (**27**) reacts with MX (M = Ag, X = Cl, I, SCN, CN; M = Cu, X = Cl, I), to afford donor-acceptor type complexes. The tin(II) [$(R^2)_2Sn\rightarrow(\mu\text{-}AgCl)]_2$ (**91**) has been characterized by X-ray structure analysis. Tin(II) complex [$(R^2)_2Sn$] (**27**) undergoes oxidative-addition reaction with AgNCO to give the oxidative-addition compound [$(R^2)_2SnNCO_2$] (**97**).

摘要

本論文工作主要包括三部分 : (i) 含氮雜烯丙基配体[$\bar{N}(SiMe_3)C(Ph)C-(SiMe_3)C_5H_4N$-2] ($\bar{R}^1$) 的低价十四族金屬有機化合成的合成與表征 ; (ii) 十四族低价金屬有機化合物的反應的活性 ; 以及 (iii) 含官能化烷基的化合物 [$Sn(R^2)_2$] (**27**) 的鹵化反應化學 .

第一章概括了十四族金屬有機化合物的化學 , 併對二价烯胺基鍺化合物[$Ge(R^1)(R^{1'})$] (**29**) , 二价胺基錫化合物[$Sn(R^1)_2$] (**30**) 及四价二氯胺基代合物 [$Sn(R^1)_2Cl_2$] (**31**) 進行了合成與表征. 晶體衍射証明了代合物 **29** , **30** 和 **31** 的分子結構. 代合物 **29** 和 **30** 是單聚體.

第二章首先介紹了十四族硫酮化合物的合成及反應活性 . 研究了低价十四族化合物 **29** 及 **30** 與硫和硒的反應 . 合成併表征了相應的金屬硫酮類化合物 [$(R^1)(R^{1'})M=E$] (M = Ge, E = S (**59**), Se (**60**); M = Sn, Se (**62**), [$(R^1)_2Sn=S$] (**61**)

第三章介紹了低价十四族金屬有機化合物與十一族金屬衍生物的反應活性 . 二价錫化合物 [$(R^2)_2Sn$] (**27**) 可以與 MX (M = Ag, X = Cl, I, SCN, CN; M = Cu, X = Cl, I) 進行反應的 , 其中給體受體化合物 [$(R^2)_2Sn\rightarrow(\mu\text{-}AgCl)]_2$ (**91**) 的分子結構得到晶體衍射証明 . 二价錫化合物 [$(R^2)_2Sn$] (**27**) 與 AgNCO 反應則生成氧化加成產物 [$(R^2)_2Sn(NCO)_2$.] (**97**) .

List of Compounds

Compound's formula	*Compounds number*	*References*
Chapter 1		
$[Ge\{CH(SiMe_3)_2\}_2]$	**1**	6, 7
$[Sn\{CH(SiMe_3)_2\}_2]$	**2**	6, 7
$[Pb\{CH(SiMe_3)_2\}_2]$	**3**	6, 7
$[Si\{CH_2(NMe_2)C_6H_4\text{-}2\}_3H]$	**4**	25-27
$[Ge\{CH_2(NMe_2)C_6H_4\text{-}2\}_3H]$	**5**	25-27
$[Si\{(NMe_2)C_{10}H_6\text{-}8\}_3H]$	**6**	3
$[C_{14}H_{24}NO_6PSn]_2$	**7**	29
$[Sn\{CPh(SiMe_3)C_5H_4\text{-}2\}_2]$	**8**	14
$[Ge\{C(CH_3)_3N(CH_2)_2NC(CH_3)_3\}]$	**9**	9
$[Sn\{NCMe_2(CH_2)_3CMe_2\}_2]$	**10**	16, 21, 24
[(Tbt)(Tip)Ge]	**11**	11
$[Ge\{CH(SiMe_3)_2\}\{C(SiMe_3)_3\}]$	**12**	10
$[Ge\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2]$	**13**	12
$[Ge\{C_6H_3(2,4,6\text{-}Me_3C_6H_2)_2\text{-}2,6\}_2]$	**14**	13
$[Ge\{CPh(SiMe_3)C_5H_4\text{-}2\}_2]$	**15**	14
$[Ge\{Si(SiMePr^i_2)_3\}_2]$	**16**	15
$[Ge\{NCMe_2(CH_2)_3CMe_2\}_2]$	**17**	16, 24
$[SnCl_2\{CH(SiMe_3)_2\}_2]$	**18**	10
$[\{2,4,6\text{-}[(CH_3)_2NCH_2]_3C_6H_2\}_2O_2Ge]$	**19**	18
$[\{(Me_3Si)_2N\}_2SnCl_2]$	**20**	29
$[\{(SiMe_2)N(Et)\}_2SnCl_2]$	**21**	29
$[(NEt_2)_2SnCl_2]$	**22**	29
$[(^tBuN(CH_2)_3N^tBu)SnCl_2]$	**23**	29
trans-$[SnCl_4(Me_2Te_2)(Ph)]$	**24**	30
trans-$[SnBr_4(Me_2Te_2)(Ph)]$	**25**	30
trans-$[\{S(C(NH)NC(CH_3)_2)_2\}Sn\{(Ph)Cl\}_2]$	**26**	32
$[Sn\{CH(SiMe_3)C_9H_6\text{-}8\}_2]$	**27**	14, 38-42
$[\{LiN(SiMe_3)_2C(Ph)C(H)(C_5H_4N\text{-}2)\}_2]$	**28**	33

Compound's formula	*Compounds number*	*References*
$[\{N(SiMe_3)_2C(Ph)C(C_5H_4N\text{-}2)\}\{N(SiMe_3)\text{-}C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Ge]$	**29**	This work
$[\{N(SiMe_3)_2C(Ph)C(H)(C_5H_4N\text{-}2)\}_2Sn]$	**30**	This work
$[\{N(SiMe_3)_2C(Ph)C(H)(C_5H_4N\text{-}2)\}_2SnCl_2]$	**31**	This work
$[\{N(SiMe_3)_2C(Ph)C(H)(C_5H_4N\text{-}2)\}_2ZrCl_2]$	**32**	29
$[(Mamx)GeN_3]$	**33**	43
$[(Mamx)GeN(SiMe_3)_2]$	**34**	43
$[Sn\{C(SiMe_3)_2C_5H_4N\text{-}2\}\{N(SiMe)_2\}]$	**35**	44
$[Ge(2\text{-}\{Me_3Si\}_2C)C_5H_4NCH(PPh_2)_2]$	**36**	12
Chapter 2		
$[\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2Ge{=}S]$	**37**	8
$[\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2Ge{=}Se]$	**38**	8
$[\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2Ge{=}Te]$	**39**	8
$[(Tbt)(Mes)Ge(\mu\text{-}Se)]$	**40**	3, 9-11
$[(Tbt)(Tip)Ge{=}S]$	**41**	3, 9-11
$[(Tbt)(Tip)Ge{=}Se]$	**42**	3, 9-11
$[\{\eta^4\text{-}Me_8taa\}Ge{=}S]$	**43**	12
$[\{\eta^4\text{-}Me_8taa\}Ge{=}Se]$	**44**	12
$[\{\eta^4\text{-}Me_8taa\}Sn{=}S]$	**45**	13
$[\{\eta^4\text{-}Me_8taa\}Sn{=}Se]$	**46**	13
$[Ge\{N(SiMe_3)_2\}_2\text{-}(\mu\text{-}S)]_2$	**47**	14-16
$[Ge\{N(SiMe_3)_2\}_2\text{-}(\mu\text{-}Se)]_2$	**48**	14-16
$[Sn\{N(SiMe_3)_2\}_2\text{-}(\mu\text{-}S)\}]_2$	**49**	14-16
$[Sn\{N(SiMe_3)_2\}_2\text{-}(\mu\text{-}Se)]_2$	**50**	14-16
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2Sn(\mu\text{-}S)]_2$	**51**	17
$[\{^tBuSn(\mu\text{-}S)\}_2]$	**52**	18
$[\{^tBuSn(\mu\text{-}Se)\}_2]$	**53**	18
$[\{^tBuSn(\mu\text{-}Te)\}_2]$	**54**	18
$[(Tbt)(Tip)Sn{=}S]$	**55**	10
$[\{(Tbt)(Tip)Sn(\mu\text{-}S)\}_2]$	**56**	10

Compound's formula	*Compounds number*	*References*
$[\{(Tbt)(Tip)Sn(\mu\text{-}Se)\}_2]$	**57**	10
$[\{(Tbt)(Mes)Sn(\mu\text{-}S)\}_2]$	**58**	10
$[\{N(SiMe_3)_2C(Ph)C(C_5H_4N\text{-}2)\}$-$\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Ge{=}S]$	**59**	This work
$[\{N(SiMe_3)_2C(Ph)C(C_5H_4N\text{-}2)\}$-$\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Ge{=}Se]$	**60**	This work
$[\{N(SiMe_3)_2C(Ph)C(H)(C_5H_4N\text{-}2)\}_2Sn{=}S]$	**61**	This work
$[\{N(SiMe_3)_2C(Ph)C(C_5H_4N\text{-}2)\}$-$\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Sn{=}Se]$	**62**	This work
$[\{CPh(SiMe_3)C_5H_4\text{-}2\}_2Ge{=}Se]$	**63**	19
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2Sn{=}Se]$	**64**	17, 19
Chapter 3		
$[Cr(CO)_5Sn(Bsi)_2]$	**65**	2-4
$[Mo(CO)_5Sn(Bsi)_2]$	**66**	2-4
$[Ge\{C_6H_3(NMe_2)_2\text{-}1,2\}_2]$	**67**	6
$[Sn\{C_6H_3(NMe_2)_2\text{-}1,2\}_2]$	**68**	6
$[\{C_6H_3(NMe_2)_2\text{-}1,2\}_2Ge\text{-}BH_3]$	**69**	6
$[\{C_6H_3(NMe_2)_2\text{-}1,2\}_2Sn\text{-}BH_3]$	**70**	6
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2Sn{\rightarrow}SnCl_2]$	**71**	7-8
$[\{CH(SiMe_3)C_9H_6\text{-}8\}SnCl]$	**72**	7-8
$[Cu(SnCl_3)(PMe_3)_3]$	**73**	9-10
$[Cu(Sn(I)Cl_2)(PMe_3)_3]$	**74**	9-10
$[Ag(PPh_3)SnCl_3]$	**75**	9-10
$[(C_6H_5)_3P_3CuCl_3]$	**76**	11
$[(C_6H_5)_3P_3AgCl_3]$	**77**	11
$[(C_6H_5)_3P_3AuCl_3]$	**78**	11
$[ClSn\{(CH_2)_n\}_3SnCl]$ n = 6, 8, 10, 12	**79**	12
$[\{Ag(SCN)Sn(Bsi)_2\}\text{-}(thf)_2]$	**80**	13
$[\{(1/n)Ag(CN)Sn(Bsi)_2\}_n]$	**81**	13

Compound's formula	*Compounds number*	*References*
$[Sn\{CH_2C(Me)=C(Me)CH_2\}]$	**82**	1
$[(Tbt)(Tip)Sn\{CH_2C(Me)=C(Me)CH_2\}]$	**83a**	17
$[(Tbt)(Tip)Sn\{OC(Ph)=C(Ph)O\}]$	**83b**	17
$[\{2,4,6\text{-}(Pr^i)_3C_6H_2\}_2Sn\{1,2\text{-}O_2\text{-}3,5\text{-}(Bu^t)_2C_6H_2\}]$	**84**	20
$[(Bsi)_2Sn(NCO)_2]$	**85**	13
$[(Bsi)_2Sn(I)_2]$	**86**	13
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2SnF_2]$	**87**	7-8
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2SnCl_2]$	**88**	7-8
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2SnBr_2]$	**89**	7-8
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2SnI_2]$	**90**	7-8
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2Sn\rightarrow(\mu\text{-}AgCl)]_2$	**91**	This work
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2Sn\rightarrow(\mu\text{-}AgI)]_2$	**92**	This work
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2Sn\rightarrow(\mu\text{-}AgSCN)]_2$	**93**	This work
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2Sn\rightarrow(\mu\text{-}AgCN)]_2$	**94**	This work
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2Sn\rightarrow(\mu\text{-}CuCl)]_2$	**95**	This work
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2Sn\rightarrow(\mu\text{-}CuI)]_2$	**96**	This work
$[\{CH(SiMe_3)C_9H_6\text{-}8\}_2Sn(NCO)_2]$	**97**	This work
$[\{(C_6H_{11})_3P\}Ag(\mu\text{-}Cl)_2Ag\{P(C_6H_{11})_3\}]$	**98**	24
$[\{(C_6H_{11})_3As\}Ag(\mu\text{-}Cl)_2Ag\{As(C_6H_{11})_3\}]$	**99**	24

Abbreviations

Ar	aryl
br	broad (spectral)
Bsi	bis(trimethylsilyl)methyl
Bu^t	*tert*-butyl
Calcd.	Calculated
cot	cyclooctatetranene
Cp	cyclopentadienyl
d	double (spectral)
dd	double of doublet (spectral)
dec	decomposed
dt	doublet of triplet
EI	electron impact (mass spectrometry)
Et	ethyl
Et_2O	diethyl ether
FT	fourier transform
Hz	hertz
IR	infra-red spectroscopy
J	coupling constant (spectral)
LDA	lithium diisopropylamide
m	multiplet (spectral)
M	parent peak
Me	methyl
Mes	2,4,6-trimethylphenyl

Me_8taa	octamethyldibenzotetraaza[14]annulene
m.p.	melting point
MHz	megahertz
MS	mass spectroscopy
m/z	mass to charge ratio (mass spectroscopy)
NMR	nuclear magnetic resonance
OAc	acetate
Ph	phenyl
Pr^i	isopropyl
Py	pyridyl
q	quartet (spectral)
s	singlet (spectral)
t	triplet (spectral)
td	triplet of doublet (spectral)
Tbt	2,4,6-tris[bis(trimethylsilyl)methyl]phenyl
THF	tetrahydrofuran
Tip	2,4,6-triisopropylphenyl
tmeda	*N,N,N',N'*-tetramethylethylenediamine
Mamx	methylaminomethyl-m-xylyl
HMPA	Hexamethylphosphoric Triamide

Chapter 1 Synthesis and Structures of Low-valent Group 14 Organometallic Compounds

1.1 General aspects of low-valent group 14 compounds

The stability of lower oxidation state (by two units) of heavier elements increases down the group for group 14 elements is due to "Inert-Pair Effect". The 1st and 2nd Ionization energies of group 14 elements have shown that apart from the +4 oxidation state, the +2 oxidation state is found to be more stable for the heavier elements.[1]

Singlet carbenes such as $:CX_2$ (X= H, R, F, Cl, Br, etc.) are reactive intermediates in organic reactions.[2] They have six electrons in the valence shell and the electron lone pair is non-bonding. Therefore, bivalent group 14 metal compounds can be regarded as carbene analogues as they posses the above properties for a carbene: The non-bonding electron pair occupies one orbital with antiparallel spins (i.e. singlet, $^1\sigma^2$).[3-5] Bivalent silicon, germanium, tin and lead compounds are so called silylenes, germylenes, stannylenes and plumbylenes, respectively. However, they behave quite differently to carbene in one common property, the energetically most favorable electron state is the singlet ($^1\sigma^2$).

Over the past two decades, it has been realized that carbene analogues such as ML_2 (M = Ge, Sn and Pb; L = general ligands like alkyls or amides) are not stable in ambient temperatures and usually form metal-metal bonded cyclic oligomers, $(R_2M)_n$. Most of them are formed at high temperatures and low pressures. Thus, stable carbene analogues are mostly prepared by using electron-releasing groups or sterically demanding substituents on the metal. The electron-releasing substituents may exert a simple inductive σ-effect (**A**), or mesomeric π-effect (**B**) or via both effects as shown in Figure 1.1.

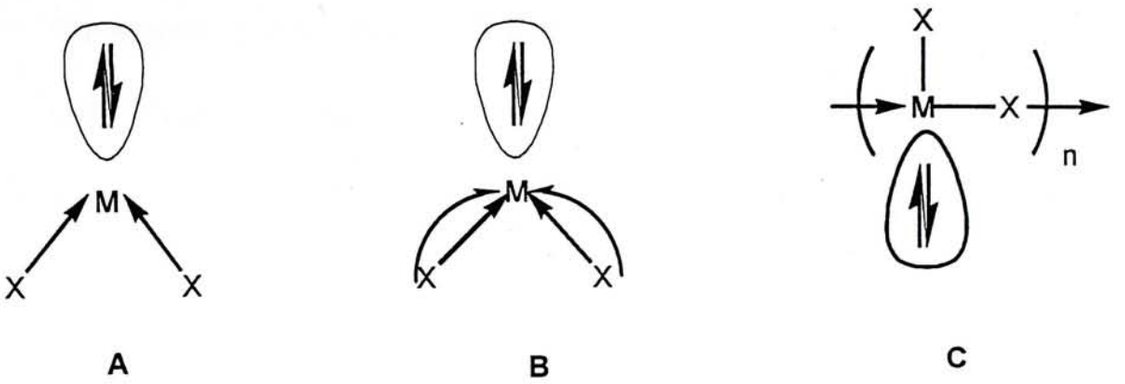
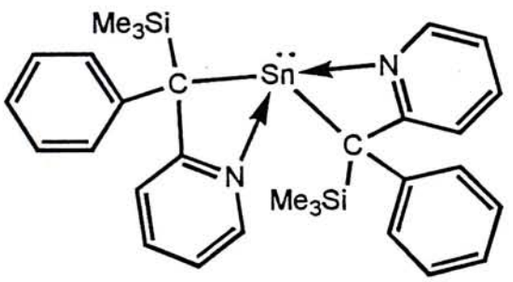


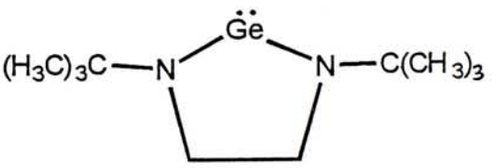
Figure 1.1

The first stable metal dialkyls $[M\{CH(SiMe_3)_2\}_2]$[6-7] [M = Ge (**1**), Sn (**2**) or Pb (**3**)] were reported by Lappert and coworkers. These compounds exist as dimers with M-M interaction in the solid state but as monomers in gas phase and solution state at ambient temperatures.

The synthesis of Group 14 germanium(II), tin(II), and lead(II) compounds are usually carried out by the reaction of the metal dihalide with 2 equivalents of an organolithium or a Grignard reagent.[8] For examples, compounds **8** and **9** were prepared using this method.[9]



(8)



(9)

1.2 Structures of germylenes and stannylenes

Germanium(II) compound **1** can be synthesized by the reaction of $GeCl_2$.dioxane with the Grigard reagent (Equation I-1).[10]

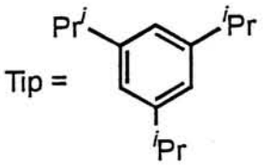
$$GeCl_2.\text{dioxane} \xrightarrow[\text{or } 2MgCl[CH(SiMe_3)_2](OEt_2),\ OEt_2]{Mg[CH(SiMe_3)_2]_2(OEt_2),\ OEt_2} Ge[CH(SiMe_3)_2]_2 \quad \textbf{1} \qquad \text{(I-1)}$$

Diarylgermylene **11** has been obtained by treatment of LiTb with germanium(II) iodide in the presence of HMPA at -78 °C followed by the addition of TipLi/THF (Equation I-2).[11]

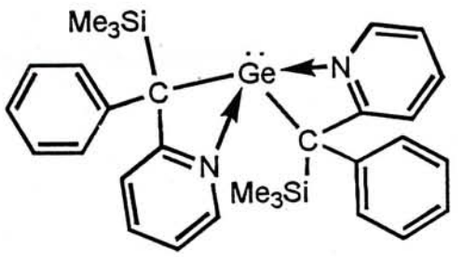
$$GeI_2 \xrightarrow[\text{2. LiTip}]{\text{1. LiTb}} \text{Tb}(\text{Tip})\text{Ge:} \quad \textbf{11} \qquad \text{(I-2)}$$

Tb =

Tip =



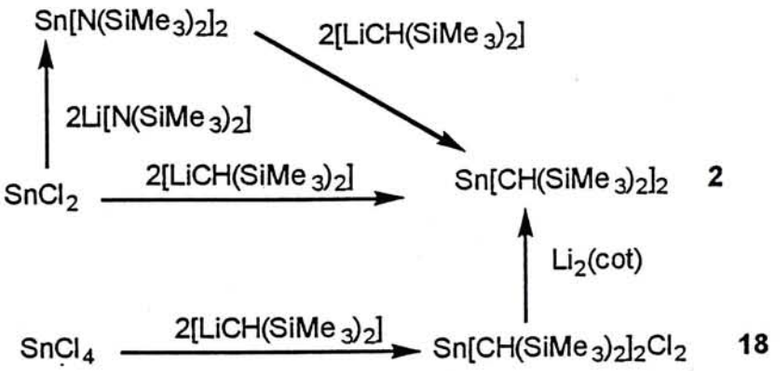
Other examples of germylenes such as $[Ge\{CH(SiMe_3)_2\}C(SiMe_3)_3]$[10] (**12**), $[Ge\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2]$[12] (**13**), $[Ge\{C_6H_3(2,4,6\text{-}Me_3C_6H_2)_2\text{-}2,6\}_2]$[13] (**14**), $[Ge\{CPh(SiMe_3)C_5H_4N\text{-}2\}_2]$[14] (**15**) have been reported. Some of these compounds exist as dimer with Ge-Ge interactions in the solid state such as $[Ge\{Si(SiMePr^i_2)_3\}]_2$[15] (**16**). $[Ge\{NCMe_2(CH_2)_3CMe_2\}_2]$ (**17**) was prepared by the reaction of $GeCl_2$.dioxane with the corresponding organolithium reagent obtained exists as monomer in solid state (Equation I-3).[16,24]



(15)

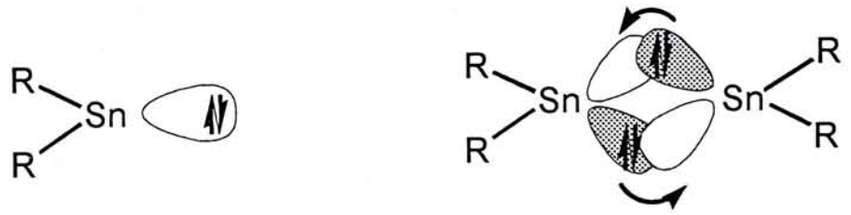
$$GeCl_2.dioxane + 2LiNCMe_2(CH_2)_3CMe_2 \xrightarrow[n\text{-}C_5H_{12}]{20\ ^\circ C} Ge[NCMe_2(CH_2)_3CMe_2]_2 \qquad \textbf{17} \qquad (I\text{-}3)$$

Two types of organostannylene have been isolated as crystalline solid and found to be thermally stable. They are (i) π-bonded dicyclopentadienyl compounds, such as $Sn(\eta^5\text{-}C_5H_5)_2$, (ii) σ-bonded, related to carbenes :CX_2 chemistry,[2] such as $[Sn(Bsi)_2]$ (**2**). The synthetic routes to $[Sn(Bsi)_2]$ are shown in **Scheme 1.1**.[10]



Scheme 1.1

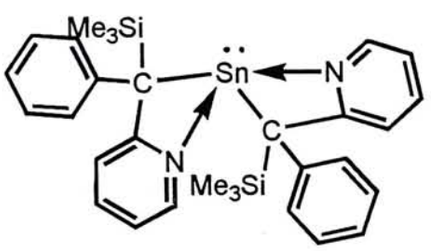
Compound **2** is monomeric in solution but dimeric in the solid state with a Sn-Sn bent double bond as illustrated in Figure 1.2.[10,17]

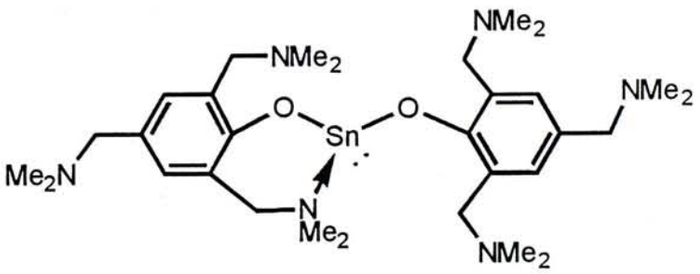


Monomer **Dimer**

Figure 1.2

Tin(II) compound [Sn{C(Ph)($SiMe_3$)C_5H_4N-2}$_2$] (**8**) can be prepared from the reaction of [{C(Ph)($SiMe_3$)C_5H_4N-2}{Li(tmeda)}] and tin(II) chloride, obtained as a reddish-yellow solid.[14] It is monomeric both in solid state and in solution state. In addition, stannylenes with ligand that is capable of intra-molecular coordination such as **8** and **19** have been reported.[18] Compound **19** was prepared in a similar way by the reaction of tin(II) chloride and aryllithium at ambient temperature.





8 **19**

Table 1.1. Structural data of some group 14 compounds

Compounds	*M-C (Å)*	*M-N (Å)*	*C-M-C (°)*	*N-M-N (°)*	*References*
$[Ge\{CH(SiMe_3)_2\}_2]_2$[a] (**1**)	2.31		107		10
$GeMe_2$[b]	2.02		98		19, 20
$Ge[CPh(SiMe_3)C_5H_4N\text{-}2]_2$ (**15**)	2.14	2.31	105.4	64.1	14
$Ge[N(SiMe_3)_2]_2$		1.89		101	15, 21, 22
$Ge[NCMe_2(CH_2)_3CMe_2]_2$ (**17**)		1.89 (av.)		111.4	21
$[Sn\{CH(SiMe_3)_2\}_2]_2$[a]	2.22		97		10
$SnMe_2$[b]	2.20		96		19, 20
$Sn[CPh(SiMe_3)C_5H_4N\text{-}2]_2$	2.33	2.45	103.6	60.3	14
$Sn[N(SiMe_3)_2]_2$		2.09		104.7, 96	10, 22, 23
$Sn[NCMe_2(CH_2)_3CMe_2]_2$ (**10**)		2.11, 2.09		109.7, 117.8	16, 21, 24

[a] gas-phase electron diffraction.

[b] Calculated value

It has been shown that Ge-C bond distance and C-Ge-C angle of $GeMe_2$ are 2.02 Å and 98° respectively and the ν (Ge-C) are 560 cm^{-1} (A_1) and 497 cm^{-1} (B_1). The calculated vibrational frequency agrees reasonably well with the experimental values from matrix-isolated species (527 and 541 cm^{-1}).[19,20]

The solid state dimeric structure of $[Ge_2\{CH(SiMe_3\}_4)]$[10] (**1**) had been confirmed by X-ray diffraction. It was found that the dimer (**1**) dissociated to $[Ge\{CH(SiMe_3)_2\}_2]$ in solution. The Ge-C bond distance of 2.31 Å and the C-M-C angle of 107° were determined by gas-phase electron diffraction. The crystal structure of $[Ge\{CPh(SiMe_3)C_5H_4N\text{-}2\}_2]$[14] (**15**) has shown that the ligand is bonded to Ge through *C,N*-chelation. The Ge-C bond distance and the C-Ge-C bond angle are 2.14 Å and 105.40° respectively. It has a square-pyramidal geometry.

For the germanium amide, $Ge[N(SiMe_3)_2]_2$, the Ge-N distance and bond

angle are 1.89 Å and 101°, while for $Ge[NCMe_2(CH_2)_3CMe_2]_2$ (**17**), the Ge-N bond distance is 1.89 Å (av.) and the N-Ge-N bond angle is 114°. The difference in N-Ge-N angle may be due to steric congestion at the ligand in compound **17**.[21]

Based on theoretical calculation of $SnMe_2$, the Sn-C distance and C-Sn-C angle were found to be 2.20 Å and 95.3° respectively.[19,20] For $[Sn(Bsi)_2]_2$ (**2**), [Bsi = $CH(SiMe_3)_2$], the bond angle and bond distance were found to be 97° and 2.22 Å respectively.[10] It was found that the data in the gas-phase structure were comparable to those values of 2.281 Å and 98.3° in the solid-state structure of $[Sn\{2,4,6\text{-}(CF_3)_3C_6H_2\}_2]$.

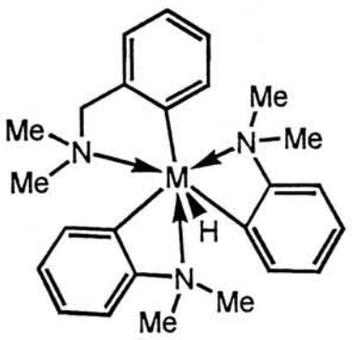
In Sn(II) compounds, SnR_2 [$\bar{R}$ = $\bar{C}Ph(SiMe_3)C_5H_4N$-2; $\bar{N}(SiMe_3)_2$], the functionalized ligand R [$\bar{C}Ph(SiMe_3)C_5H_4N$-2] is bonded to the Sn through a *C,N*-chelation, while the structure of $Sn[N(SiMe_3)_2]_2$ is a V-shaped monomer with C_{2v} symmetry.[1,22,23] The structure of $[Sn\{CPh(SiMe_3)C_5H_4N\text{-}2\}_2]$ (**8**) showed a square-pyramidal geometry consistent with a stereoactive lone pair at the metal center.[14]

1.3 Tetravalent group 14 metal amides

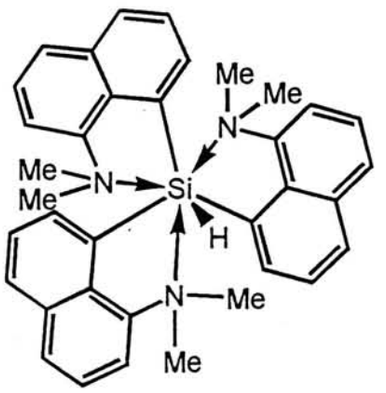
Organotin(IV) compounds usually act as a synthetic precursor to functionalized chemical reactions. They are mostly colorless solid and stable in air. The structures of organotin(IV) compounds are based on tetrahedral coordination and an octahedral geometry in the molecular compounds. Group 14 metal compounds **4-6** contain silicon- and germanium- carbon bonds are known.[3]

The larger atomic size of Sn allows the extension of a higher coordination number above 6, including both the +2 and +4 state. They can achieve higher coordination number by using the vacant orbitals. Functionalized alkyl or amide ligands with donor atom can influence both reactivities of M-C and M-N bond by forming chelating ring. Compounds **4-7** are some examples of hypervalent silicon,

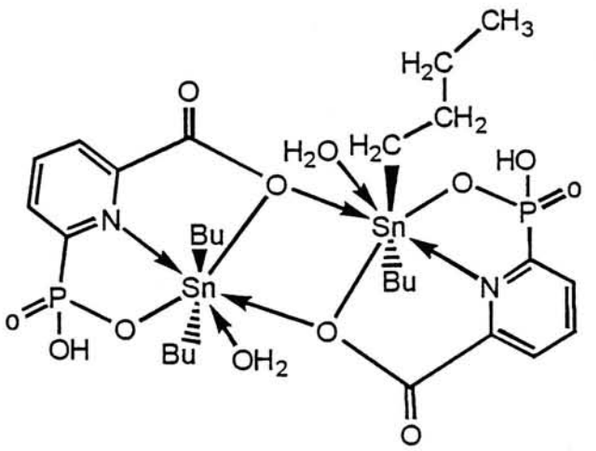
germanium and tin complexes.[8,25-28]



(4) M= Si
(5) M= Ge



(6)



(7)

Organotin(IV) compounds can be prepared by Kocheshkov redistribution reaction between a tetraorganotin and a tin(IV) halide.[2] With appropriate choice of reaction stoichiometry, mono, di-, or triorganotin halide can be obtained. (**Scheme 1.2**).

$$3R_4Sn + SnCl_4 \longrightarrow 4R_3SnCl$$

$$R_4Sn + SnCl_4 \longrightarrow 2R_2SnCl_2$$

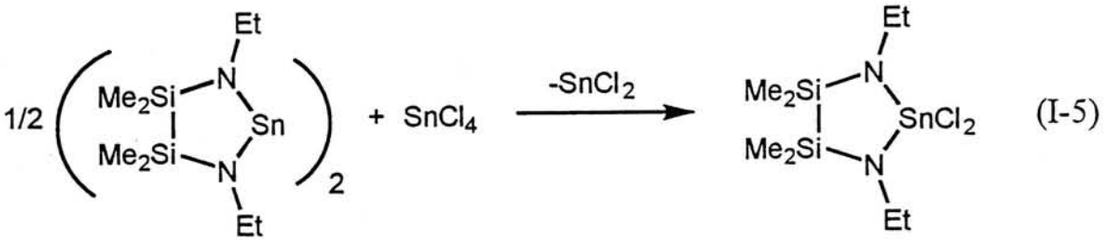
$$R_4Sn + 3SnCl_4 \longrightarrow 4RSnCl_3$$

Scheme 1.2

Other routes to organotin(IV) chlorides are by the reaction between tin(IV) chloride and tin(II) amide as shown in Equations I-4 and I-5.

$$[(Me_3Si)_2N]_2Sn + SnCl_4 \xrightarrow{-SnCl_2} [(Me_3Si)_2N]_2SnCl_2 \qquad \text{(I-4)}$$

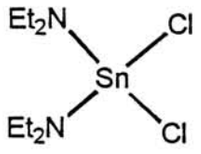
20



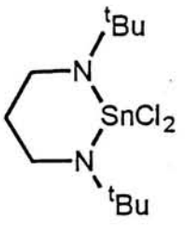
(I-5)

21

Compound **20** is a monomeric tin(IV) diamide dichloride while compound **21** is a cyclic tin(IV) diamide dichloride. Organotin(IV) chlorides of compounds **22** and **23** were also obtained similarly.[29]

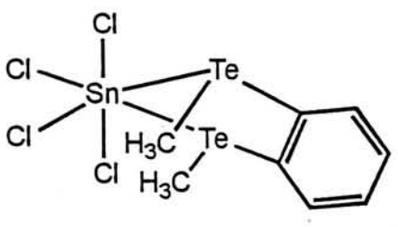


22

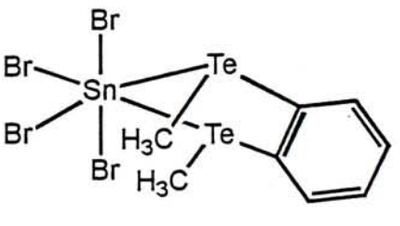


23

Compounds **24** and **25** were tin(IV) halides of telluroether adducts obtained by reaction of SnX_4 (X = Cl, Br) with mono- or di-telluroether ligands.[30]

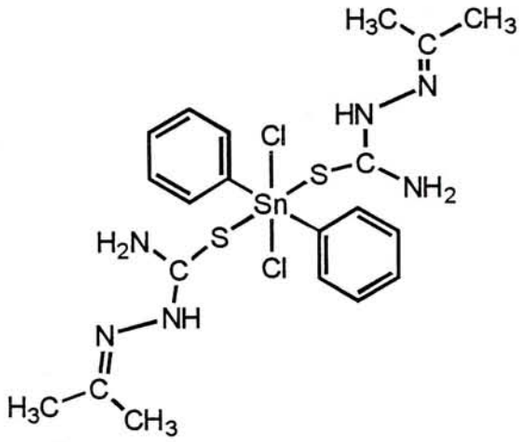


24



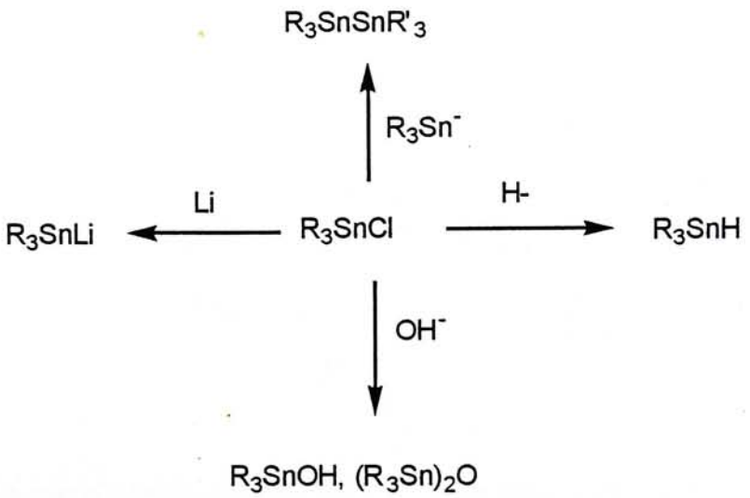
25

In the far IR spectrum of **24**, the peak at 312 cm^{-1} is consistent with a *trans* geometry when compared with the peak of 312 cm^{-1} in *trans*-$[SnCl_4(Me_2Se_2)(Ph)]$.[31] The structural studies of compound **24** and **25** had shown a distorted octahedral tin(IV) which is mostly found in Sn(IV) halide structures. Compound **26** was obtained with a distorted octahedral geometry, the Cl-Sn-Cl bond angle being 180°. The Sn-Cl bond distance of 2.59 Å (av.)[32] is longer than that of the Sn-Cl bond distance of 2.38(2), 2.39(2), 2.43(2) and 2.46(2) Å in compound **24**.



26

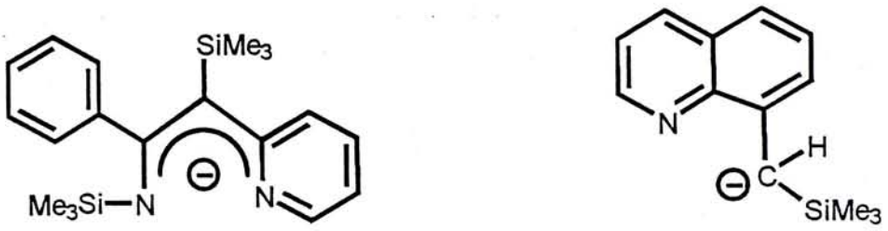
Organotin(IV) halides can be prepared by the reaction of a lithium reagent with $SnCl_4$. For example, $[Sn\{CH(SiMe_3)_2\}_2Cl_2]$ (**18**) in **Scheme 1.1**. The organotin halides can undergo a wide range of nucleophic substitution reactions, some examples are shown in **Scheme 1.3**.



Scheme 1.3

1.4 Objectives

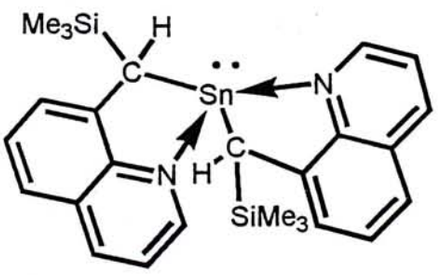
The objectives of this work can be divided into three parts. The first part is to synthesize some thermally stable Group 14 metal compounds. The second part is to investigate the reactivities of some low-valent group 14 compounds. The third part is to investigate the reactivities of some halogenated derivative of group 14 complexes. In this work, ligand ($\bar{R}^1$)[33-37] (Figure 1.3) will be used to synthesize low-valent group 14 compounds.



$^-R^1$ $^-R^2$

Figure 1.3

The *N,N'*-monoanionic azaally ligand $\bar{R}^1$ can accommodate a wide range of metal size through different bonding modes. The two nitrogens can form a chelate, which also have additional stabilization effect on the resultant metal amide complexes. The reactivity of the thermally stable Sn(II) dialkyl **27** previously isolated and structurally characterized in our group using the alkyl ligand ($\bar{R}^2$) will be investigated.[13,38-42]



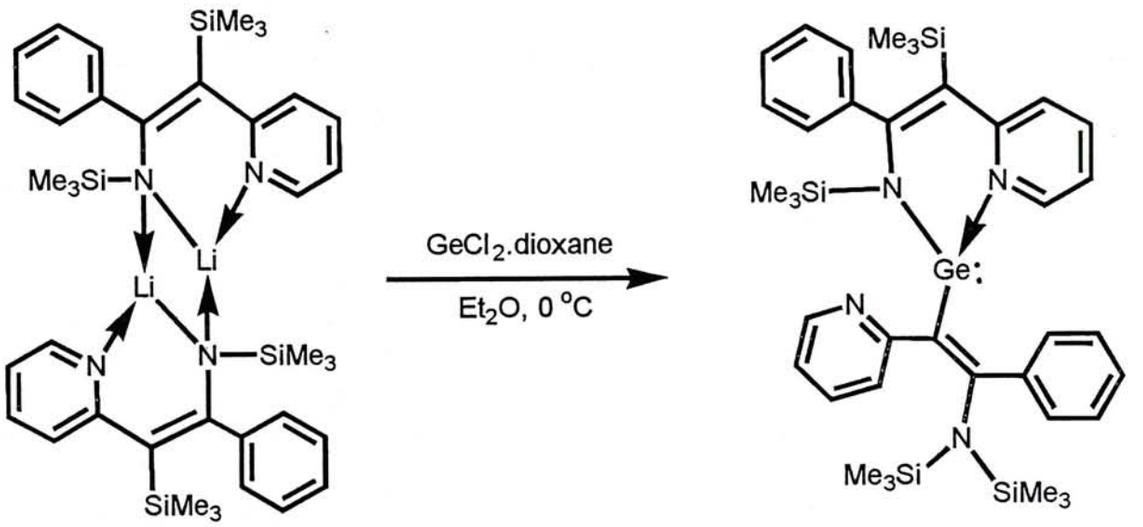
27

The Group 14 metal amide complexes that have been synthesized will be structurally characterized by single X-ray diffraction studies and spectroscopic methods.

1.5 RESULTS AND DISCUSSION

1.5.1 Synthesis of germanium(II) compound [Ge{C(C_5H_4N-2)C(Ph)N-($SiMe_3$)$_2$}{N{($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}] (29)

Treatment of two equivalents of the lithium complex [Li{N($SiMe_3$)C(Ph)-C($SiMe_3$)(C_5H_4N-2)}]$_2$[33] with $GeCl_2$.dioxane in ether afforded hydrocarbon soluble germanium(II) (alkenyl)amide [Ge(R$^{1'}$)(R^1)] (**29**) in 62% yield (**Scheme 1.4**).

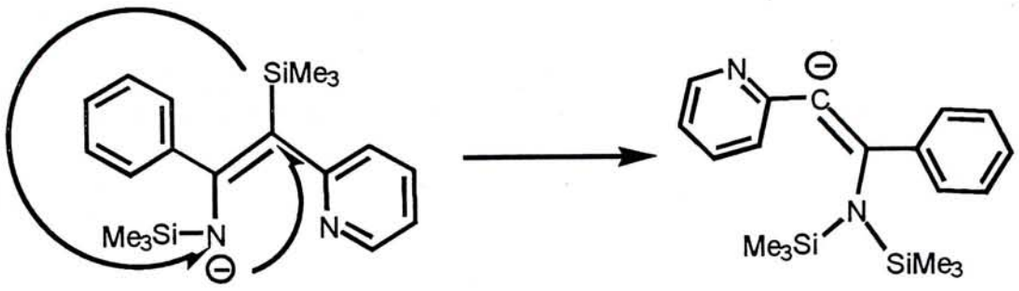


28 **29**

Scheme 1.4

Compound **29** was isolated as air-sensitive orange crystals (m.p. 206-208 °C (dec.)). The structure of **29** has been determined by single crystal X-ray crystallography (Figure 1.4). It has shown that one of the ligands is bonded to the central germanium atom via *N,N'*-chelation, while the other ligand is bonded to the germanium atom via the β-carbon. This is a consequence of rearrangement of the azaallyl ligand together with 1,3 shift of the $SiMe_3$ group (Equation I-6). The phenyl ring is *trans* to the pyridyl ring. The shifting is presumably due to the smaller size of germanium atom (as compared to tin) that allowed it to have a less steric

crowding environment.

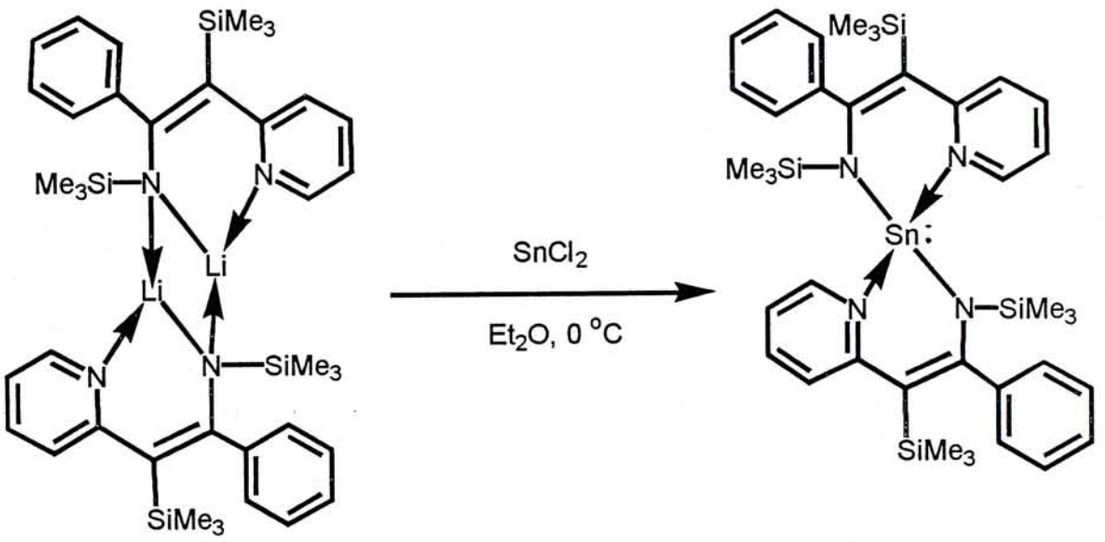


(I-6)

Monomeric heteroleptic derivatives of Ge(II) are extremely rare. Some of these compounds have been detected but not structurally characterized due to their instability in solution. Compounds like [(Mamx)GeN_3] (**33**) and [(Mamx)-$GeN(SiMe_3)_2$] (**34**) [Mamx: (methylaminomethyl-m-xylyl)] are some examples of heteroleptic Ge(II) derivatives. They were prepared from the reaction of (Mamx)GeCl, NaN_3 and $LiN(SiMe_3)_2$.[43] Heteroleptic (chiral) Sn(II) alkyls and amides, Sn(R)X [$\bar{R} = \bar{C}(SiMe_3)_2C_5H_4N$-2; $X = \bar{N}(SiMe_3)_2$] (**35**) had been reported in 1979. It was a plausible model for isoleptic Ge(II) and Pb(II) alkyls.[44] Recently, germanium(II) compound [Ge{2-$(Me_3Si)_2C$}$(C_5H_4N)CH(PPh_2)_2$] (**36**) which contains two ligands with different bonding modes (η^1, C-bound and η^2, P-bound) within the same molecules had been reported. It was prepared by reaction of $Li(Et_2O).CH(PPH_2)$ and [Ge(2-{$(Me_3Si)_2C$}$(C_5H_4N)Cl$].[45]

1.5.2 Synthesis of tin(II) amides [Sn{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$] (30)

Reaction of lithium complex [Li{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}]$_2$ (**28**) with tin(II) dichloride in ether afforded compound **30** in 52% yield (**Scheme 1.5**).



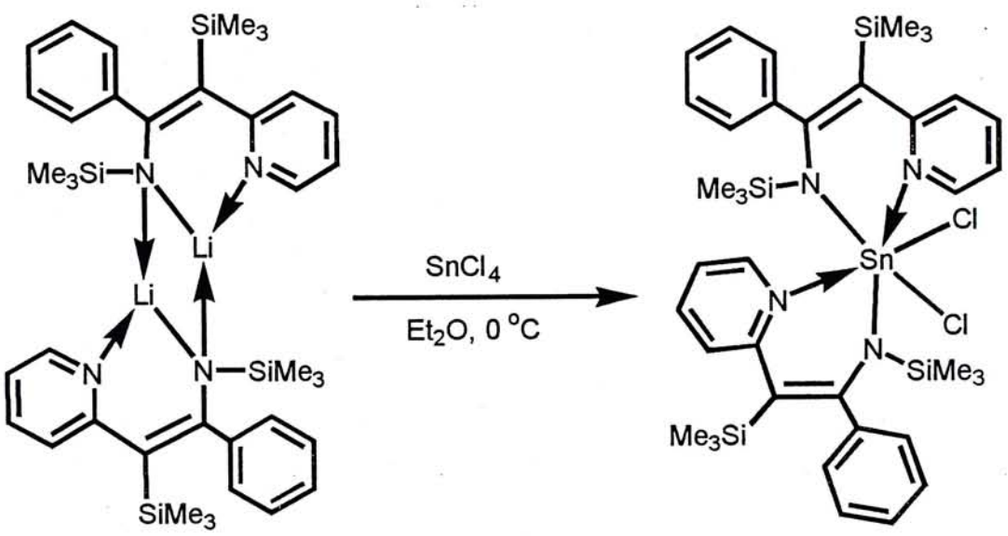
28 **30**

Scheme 1.5

Compound **30** is soluble in hydrocarbon solvents such as toluene, hexane and pentane and polar solvents such as ether and THF, but decomposes in CH_2Cl_2 and $CHCl_3$. Compound **30** was isolated as an air-sensitive yellow crystalline solid (m.p. 148-151 °C (dec.)). The structure of **30** has been determined by single crystal X-ray crystallography (Figure 1.5) and it was found to be different from that of the Ge(II) analogue (**29**). The two *N,N'*-dianionic ligands are bonded to the central tin atom via *N,N'*-chelation.

1.5.3 Synthesis of tin(IV)(amide)dichloride [Sn{N(SiMe$_3$)C(Ph)C(SiMe$_3$)-(C$_5$H$_4$N-2)}$_2$Cl$_2$] (31)

The reaction of [Li{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}]$_2$ with SnCl$_4$ afford [Sn{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$Cl$_2$] (**31**) in 58% yield (**Scheme 1.6**). Compound **31** is air stable and soluble in THF, ether, and toluene but decomposes in CH_2Cl_2 and $CHCl_3$.



28 **31**

Scheme 1.6

1.5.4 Spectroscopic properties of Compounds 29-31

Compound **29-31** were characterized by microanalysis, mass spectrometry, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. The physical properties and microanalysis data for compounds **29-31** are shown in Table 1.2.

Table 1.2. Physical properties and microanalysis of compounds 29-31

Compounds	*Appearance*	*m.p. °C*[a]	*Yield %*	*Microanalysis % C, H, N*[b]
$Ge(R^{1'})(R^{1})$ (**29**)	Orange crystals	206-208 (dec.)	62	60.69, 7.19, 7.70 (60.75, 7.19, 7.46)
$Sn(R^{1})_2$ (**30**)	Yellow crystals	148-151 (dec.)	52	57.20, 6.82, 7.02 (56.82, 6.83, 6.94)
$Sn(R^{1})_2Cl_2$ (**31**)	Yellow crystals	227-230 (dec.)	58	52.51, 6.03, 6.58 (52.23, 6.26, 6.45)

[a] m.p. were measured in capillary tube sealed under nitrogen and were uncorrected.

[b] figures in parenthesis are the calculated values based on the molecular formula shown.

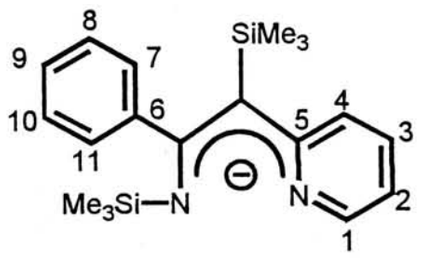
The mass spectral data for compounds **29-31** are shown in Table 1.3. The mass spectra of compounds which showed the presence of parent peaks $[M]^+$ at 752, 798, respectively for **29** and **30.** The mass spectra of compound **31** only showed peaks at 833 which is assignable to the loss of Cl^- from the parent molecule.

Table 1.3. Mass spectra data for compounds 29-31

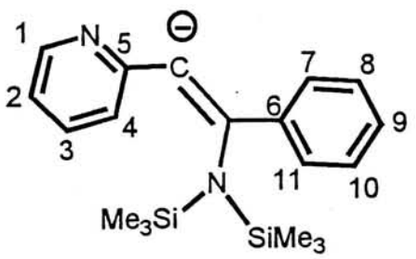
Compounds	*Parent peak [M]*$^+$	*Other important fragment peaks*
$Ge(R^{1})(R^{1'})$ (**29**)	752	412 $[M\text{-}R^{1}]^+$
$Sn(R^{1})_2$ (**30**)	798	459 $[M\text{-}R^{1}]^+$, 339 $[R^{1}]^+$
$Sn(R^{1})_2Cl_2$ (**31**)	-----	833 $[M\text{-}Cl]^+$, 798 $[M\text{-}Cl\text{-}Cl]^+$

The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectral data are shown in Table 1.4 and Table 1.5, respectively. The ^{1}H NMR spectrum of **29** displayed three singlets due to three different $SiMe_3$ groups after the rearrangement of the parent azaally ligand $\bar{R}^1$. It showed an upfield shift when compared with the lithium amide $[Li\{N\text{-}(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}]_2$. The ^{1}H NMR of **30** also showed different pattern from the lithium amide because the peaks due to the four $SiMe_3$ group and the aromatic groups are different from each other. The change in central metal coordination resulting in the displayed of upfield shift. Similar nmr pattern due to the ligand backbone was also observed in **31**.

The $^{13}C\{^{1}H\}$ NMR of **29** and **30** displayed two sets of aromatic carbons for the ligand $\bar{R}^1$ and $\bar{R}^{1'}$ and **31** showed only one sets of the 11 types of aromatic carbons (Figure 1.7).



$\bar{R}^1$



$\bar{R}^{1'}$

Figure 1.7

Table 1.4. **^{1}H NMR spectral data for compounds 28[a], 29-30[b] and 31[c].**

Compounds	*Me_3Si*	*Phenyl*	*Pyridyl*
LiR^1H^{32} (**28**)	-0.36, -0.41	7.15-7.18(m), 7.29-7.33(m)	6.68(ddd), 7.11(dt), 7.38(ddd), 8.13(ddd)
$Ge(R^1)(R^{1'})$ (**29**)	-0.04, 0.06, 0.21	7.05(m), 7.50(m)	6.52(t), 6.67(br), 7.12(br), 7.77(d), 8.59(d)
$Sn(R^1)_2$ (**30**)	-0.16, -0.03, -0.01, 0.22	7.08(m), 7.75(d)	6.49(br), 6.57(m), 7.49(m), 9.09(br)
$Sn(R^1)_2Cl_2$ (**31**)	-0.02, 0.03	6.98-7.20(m), 7.60(s)	6.09(m), 6.90(td),7.99(t), 8.5(d)

[a] chemical shifts are in δ (ppm) referenced to internal d_8-THF (δ 3.58 ppm), 250.00 MHz.

[b] referenced to internal C_6D_6 (δ 7.15 ppm), 300.13 MHz.

[c] referenced to internal C_7D_8 (δ 7.00 ppm), 300.13 MHz.

Table 1.5. $^{13}C\{^1H\}$ NMR spectral data for compounds 28[a], 29-30[b], 31[c].

Compounds	*Me_3Si*	*$CSiMe_3$*	*Aromatic Carbon*	*NCPh*
LiR^1H^{32}(**28**)	3.80	99.00	115.70, 125.80, 127.20, 127.60, 130.80, 135.00, 146.40, 151.50, 167.00	174.20
$Ge(R^1)(R^{1'})$ (**29**)	2.94, 3.02, 3.11	114.21, 155.88(N*C*Ge)	117.93, 118.98, 119.13, 123.73, 124.20, 124.96, 125.59, 127.39, 127.79, 128.33, 128.79, 129.00, 130.69, 131.13, 135.05, 136.66, 144.09, 145.31, 147.22, 147.99, 150.80, 153.57	166.79, 171.46
$Sn(R^1)_2$ (**30**)	1.38, 2.41, 3.65, 4.59	118.08, 118.77	118.87, 123.91, 124.10, 124.80, 125.64, 127.23, 127.68, 128.56, 129.28, 130.47, 131.12, 135.20, 135.58, 137.07, 141.95, 144.29, 146.06, 147.51, 147.68, 147.98, 151.68, 158.76, 159.24	168.17, 173.09
$Sn(R^1)_2Cl_2$ (**31**)	-2.78, 0.96	107.69	112.89, 119.68, 121.56, 124.58, 126.06, 130.69, 132.36, 132.66, 139.22, 140.21, 160.27	164.34

[a] chemical shifts are in δ (ppm) referenced to internal d_8-THF (δ 25.20 ppm), 250.00 MHz.

[b] referenced to internal C_6D_6 (δ 128.00 ppm), 75.47 MHz.

[c] referenced to internal C_7D_8 (δ 120.00 ppm), 75.47 MHz.

Table 1.6. **^{119}Sn NMR spectral data for compounds 30-31 and some related compounds**

Compounds	*δ, ppm*	*References*
$[Sn(R^1)_2]$ (**30**)[a]	-140.00	This work
$[Sn(R^1)_2Cl_2]$ (**31**)[b]	-82.54	This work
$Sn[CPh(SiMe_3)(C_5H_4N\text{-}2)]_2$ (**8**)[a]	141.73	18
$Sn[NCMe_2(CH_2)_3CMe_2]_2$ [b] (**10**)	749.00	20
$[Sn\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2]$ [b]	141.00	46
$[Sn\{CH_2(NMe_2)C_6H_4\text{-}2\}_2]$ [c]	169.00	47
$[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}Cl_2]$	-248.00	40

[a] recorded in C_6D_6 and referenced to external $SnMe_4$ at 298 K

[b] recorded in C_7D_8 and referenced to external $SnMe_4$

[c] recorded in THF-d_8 and referenced to external $SnMe_4$ at 313 K

The ^{119}Sn NMR spectroscopic data of compound **30**, **31** and some related Sn(II) and Sn(IV) compounds are shown in Table 1.6. The ^{119}Sn NMR chemical shift of δ -140 ppm in **30** which show more up field than $Sn[CPh(SiMe_3)(C_5H_4N\text{-}2)]_2$ (**8**) (δ 147.3 ppm), $Sn[NCMe_2(CH_2)_3CMe_2]_2$ (**10**) (δ 749 ppm), $[Sn\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2]$ (δ 141 ppm) and $[Sn(CH_2(NMe_2)C_6H_4\text{-}2)_2]$ (δ 169 ppm). The difference may be due to compound **30** contains *N,N'*-chelate to the tin atom while others are *C,N*-chelate to the tin atoms. The signal due to compound **31** was observed in a more down field region when compared with the values of Sn(IV) compound $[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}Cl_2]$ (δ -248.52).[40]

1.5.5 Molecular structure of [Ge{C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}{N($SiMe_3$)C-(Ph)C($SiMe_3$)C(C_5H_4N-2)}] (29)

The molecular structure of compound **29** has been determined by single crystal X-ray structure analysis. Projection of the molecule with atom numbering schemes is shown in Figure 1.4. Selected bond distances and angles of **29** are shown in Table 1.7.

Compound **29** consists of discrete molecules in space group $P2_1/c$ (No.4). The structure had shown that one of the ligand [$\bar{N}$($SiMe_3$)C(Ph)C($SiMe_3$)C(C_5H_4N-2)] ($\bar{R}^1$) is bonded to the germanium atom in *N,N'*-chelate fashion whereas the other ligand [N($SiMe_3$)$_2\bar{C}$(C_5H_4N-2)C(Ph)] ($\bar{R}^{1'}$) germanium atom is bonded to C(26) at a distance of 2.04(2) Å consistent with a C-centered alkenyl ligand. The germanium atom is three-coordinated, showing a distorted trigonal pyramidal geometry. The bond angles of N(2)-Ge-C(26), N(2)-Ge-N(1) and C(26)-Ge-N(1) are 105.16(8)°, 86.30(7)° and 98.54(7)° respectively. The deviation from trigonal pyramidal geometry is due to the steric hinderance of the NCCCN skeleton.

The bonding within the NCCCN ligand backbone is highly localized within PhC=C double bonds, leaving the aromaticity of the pyridyl ring largely unaffected. The Ge-N(1) and Ge-N(2) bond distances of 2.07(15) Å and 1.94(17) Å are shorter than the Ge-N bond distances of 2.30 Å (av.) in [Ge{CPh($SiMe_3$)C_5H_4N-2}$_2$][14] (**15**) and the Ge-N bond distances of 2.09(7) Å in [Ge(2-{Me_3Si}$_2$C)(C_5H_4N)CH(PPh_2)$_2$] (**36**). The Ge-C(26) bond distance of 2.04(2) Å is shorter than similar distance of 2.13 Å (av.) in [Ge{CPh($SiMe_3$)C_5H_4N-2}$_2$] (**15**) and the distance of 2.10(8) Å in [Ge(2-{Me_3Si}$_2$C)(C_5H_4N)CH(PPh_2)$_2$][45] (**36**). The GeNCCCN metallacycles are highly puckered and can be seen from the large out of plane rotation of the phenyl group to the C(13)-C(12)-C(6) plane at 121.87(17)°, which preventing steric

congestion with the C(12)-C(13) double bond. The C(26)-Ge-N(1) bond angle of 98.54(7)° in **29** is comparable to the N-Ge-C bond angle of 98.70(3)° in [Ge(2-{Me_3Si}$_2$C)(C_5H_4N)CH(PPh_2)$_2$] (**36**).[45] It is probably due to the smaller size of germanium which cannot allow both amido ligands bond to the central atom in *N,N'*-chelate fashion. As a consequence, one of the azaallyl ligand undergoes a 1,3-trimethylsilyl shift, the $SiMe_3$ at C(26) migrated to N(3). The negative charge originally localized at N-amido shifted to C(26). This migration of the substituent or migration of charge within ligand backbone allows the release of steric strain at the central atom.

Table 1.7. Selected bond distances (Å) and angles (°) for compound 29

Ge[{C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}{N($SiMe_3$)C(Ph)C($SiMe_3$)C(C_5H_4N-2) }] (**29**)

Ge-N(1)	2.065(15)	Ge-C(26)	2.039(2)
Ge-N(2)	1.942(17)	C(14)-C(26)	1.488(3)
N(2)-C(12)	1.405(2)	C(25)-C(26)	1.356(3)
C(12)-C(13)	1.357(3)	C(19)-C(25)	1.491(3)
C(13)-C(1)	1.471(3)	N(3)-C(25)	1.453(3)
Si(2)-N(2)	1.746(18)	Si(3)-N(3)	1.750(19)
Si(1)-C(13)	1.897(2)	Si(4)-N(3)	1.751(2)
N(2)-Ge-C(26)	105.16(18)	C(25)-C(26)-Ge	118.52(14)
N(2)-Ge-N(1)	86.30(7)	C(25)-C(26)-C(14)	119.6(2)
C(26)-Ge-N(1)	98.54(7)	C(14)-C(26)-Ge	118.96(13)
C(1)-N(1)-Ge	124.04(12)	N(3)-C(25)-C(19)	114.23(16)
N(1)-C(1)-C(13)	120.68(16)	C(26)-C(25)-C(19)	120.5(2)
C(12)-N(2)-Ge	118.59(13)	C(13)-C(12)-C(6)	121.87(17)
C(12)-C(13)-C(1)	119.11(17)	C(13)-C(12)-N(2)	124.23(17)

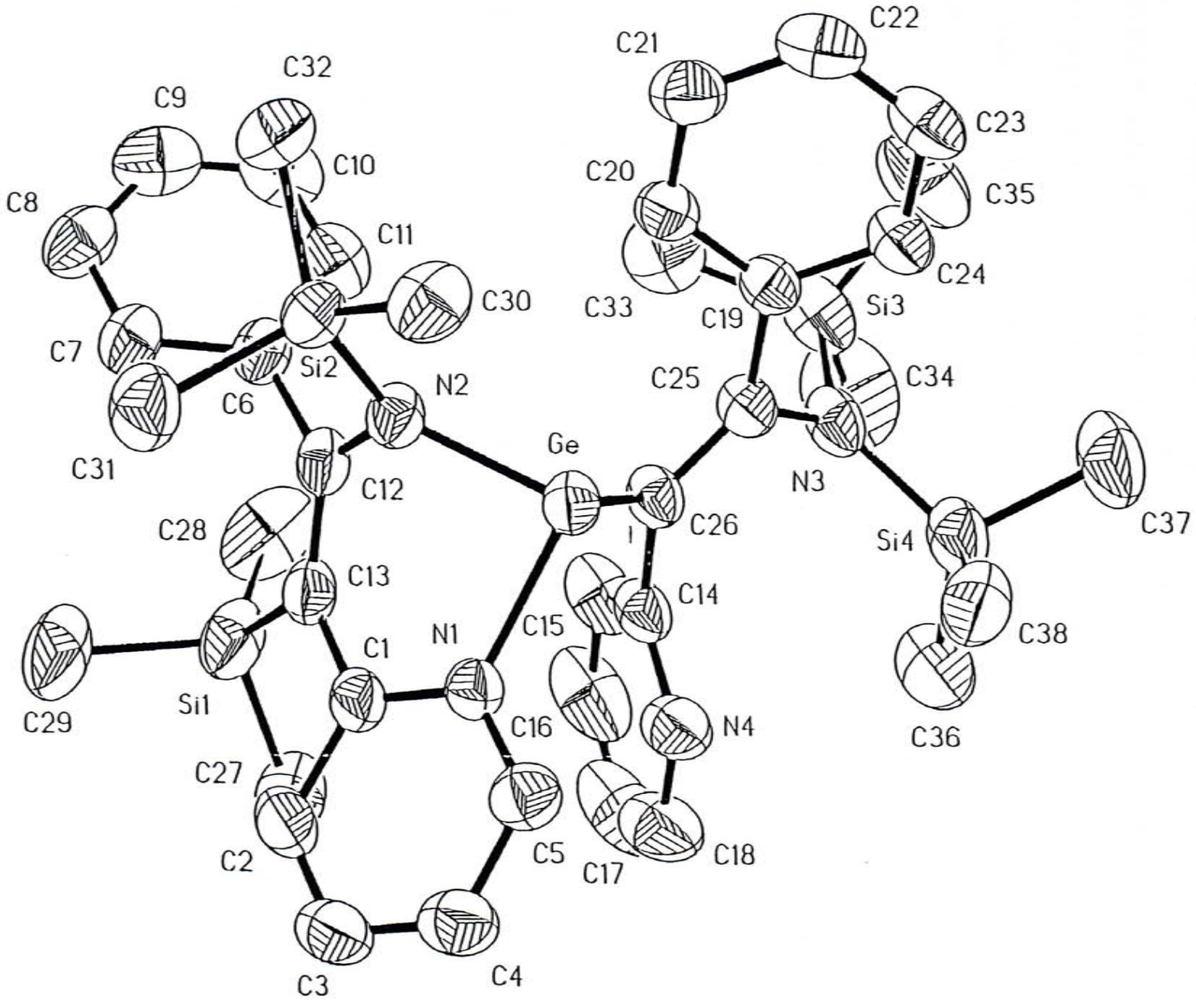


Figure 1. 4 Molecular Structure of [Ge{N(SiMe$_3$)C(Ph)C(C$_5$H$_4$N-2)}{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)$_2$}] (29)

1.5.6 Molecular structures of [Sn{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$] (30)

The molecular structure of compound **30** has been determined by single crystal X-ray diffraction studies. Projection of the molecule with atom numbering scheme is shown in Figure 1.5. Selected bond distances and angles of **30** are shown in Table 1.8. Compound **30** consists of discrete molecules in a triclinic space group $P\bar{1}$ (No. 2). The azaallyl ligand $\bar{R}^1$ is bonded in an *N,N'*-chelate fashion to the tin atom and the N_2SnN_2 unit shows a square pyramidal geometry with two pairs of nitrogen atoms in *trans* position and the Sn atom being tetra-coordinated. The negative charge is highly localized at the amido nitrogen and leaving the aromaticity of the pyridyl ring largely unaffected.

The Sn-N(pyridyl) bond distances of 2.47 Å (av.) **30** is comparatively longer than of 1.98(7) Å the Li-pyridine distance in the hexa-coordinate Li-compound [Li{N-(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}]$_2$.[33]

The SnNCCCN metallacycles are highly puckered because of the steric interactions between Ph and the SiMe$_3$ groups. It can be shown by the large out of plane rotation of the phenyl group relative to the C(6)-C(10)-C(11) plane (C(6)-C(10)-C(11)-C(16)=120°), releasing the effective conjugation.

Table 1.8. Selected bond distances (Å) and angles (°) for compound 30

[Sn{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$] (**30**)			
Sn(1)-N(2)	2.162(2)	Sn(1)-N(4)	2.174(2)
Sn(1)-N(1)	2.441(2)	Sn(1)-N(3)	2.503(2)
N(2)-C(10)	1.403(3)	N(4)-C(29)	1.384(3)
N(1)-C(5)	1.364(3)	N(3)-C(24)	1.335(3)
N(1)-C(1)	1.340(3)	N(3)-C(20)	1.343(3)
C(6)-C(10)	1.366(4)	C(25)-C(29)	1.402(3)
C(5)-C(6)	1.449(3)	C(24)-C(25)	1.457(4)
N(2)-Sn(1)-N(4)	107.72(7)	N(2)-Sn(1)-N(1)	78.08(7)
N(4)-Sn(1)-N(1)	91.26(7)	N(4)-Sn(1)-N(3)	76.69(7)
N(2)-Sn(1)-N(3)	91.58(7)	C(5)-N(1)-Sn(1)	123.8(2)
C(24)-N(3)-Sn(1)	123.8(2)	N(1)-C(5)-C(6)	121.8(2)
N(3)-C(24)-C(25)	121.7(2)	C(10)-C(6)-C(5)	120.5(2)
C(29)-C(25)-C(24)	119.9(2)	C(6)-C(10)-N(2)	126.6(2)
N(4)-C(29)-C(25)	126.0(2)	C(10)-N(2)-Sn(1)	124.0(2)
C(29)-N(4)-Sn(1)	123.9(2)		

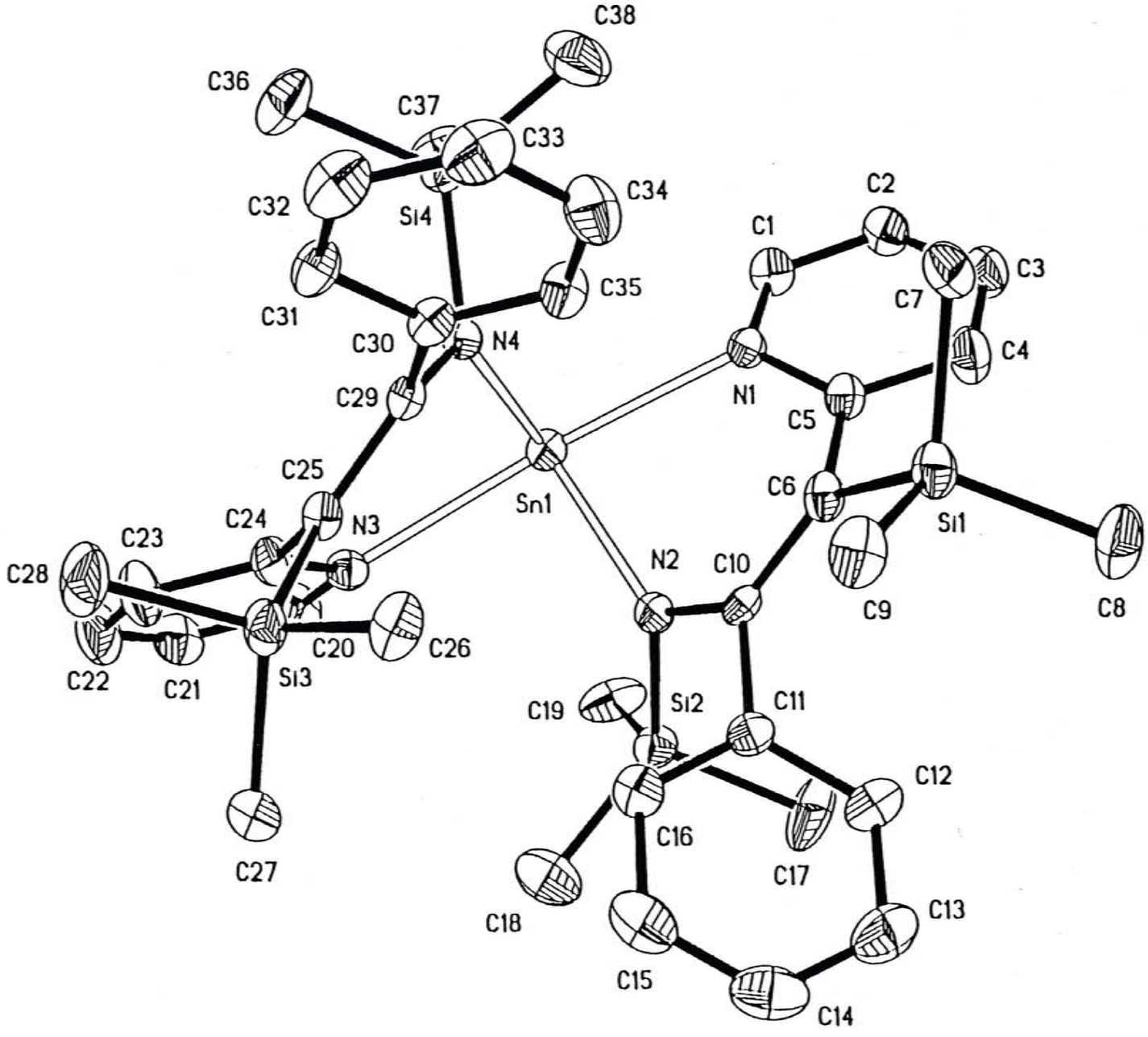


Figure 1. 5 Molecular Structure of [Sn{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$] (30)

1.5.7 Molecular structures of [Sn{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$Cl$_2$] (31)

The molecular structure of compound **31** with atom numbering schemes is shown in Figure 1.6. Selected bond distances and angles are listed in Table 1.9.

Compound **31** crystallized in a monoclinic Cc (No.4) space group. The geometry around the tin center is most appropriately described as distorted octahedral with a C_{2v} Symmetry, in which the Cl-Sn-N situated on the crystallographic C_2 axis. The two 2-pyridyl amido ligands $\bar{R}^1$ and two chlorides are in *cis* position. The central tin atom is nearly coplanar to the plane of Cl(1), Cl(2), N(1), N(3) and the atoms of Cl(1) and N(3) are in *trans*-apical position of the distorted octahedral. The N(4)-Sn(1)-N(2) angle of 173.41(7)° deviates considerably from the ideal linearity value of 180°.

Both Sn-Cl distances of 2.42 Å (av.) and the Cl(1)-Sn-Cl(2) angle of 92.79(6)° are comparable with the Sn-Cl distances of 2.45 Å and Cl(1)-Sn-Cl(2) angle of 95.4° in [{CH(SiMe$_3$)C$_9$H$_6$N-8}$_2$SnCl$_2$].[40] The Cl(1)-Sn(1)-Cl(2) plane is distorted relative to the N(1)-Sn(1)-N(3) plane by 13.71°. The bonding within the chelating NCCCN skeletons are highly localized with Sn(1)-N(1) and C(5)-C(6) single bond and C(6)-C(7) double bonds. The Sn(1)-N(1) and Sn(1)-N(3) are dative bonds and Sn(1)-N(2) and Sn(1)-N(4) are covalent bonds and pyridyl ring distances are normal. The steric interactions between Ph and SiMe$_3$ substituents result in the SnNCCCN metallacycles are highly puckered.

Table 1.9. Selected bond distances (Å) and angles (°) for compound 31

[Sn{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$Cl$_2$] (**31**)

Sn(1)-N(2)	2.112(3)	Sn(1)-N(4)	2.057(3)
Sn (1)-N(1)	2.273(2)	Sn(1)-N(3)	2.284(2)
Sn(1)-Cl(1)	2.440(10)	Sn(1)-Cl(2)	2.409(10)
N(2)-C(7)	1.373(4)	N(4)-C(29)	1.454(4)
N(1)-C(5)	1.373(4)	N(3)-C(24)	1.366(4)
N(1)-C(1)	1.370(4)	N(3)-C(20)	1.337(4)
C(6)-C(7)	1.421(4)	C(25)-C(29)	1.317(5)
C(5)-C(6)	1.418(4)	C(24)-C(25)	1.510(4)
N(4)-Sn(1)-N(2)	173.41(7)	N(1)-Sn(1)-Cl(2)	167.98(7)
N(3)-Sn(1)-Cl(1)	168.61(8)	Cl(2)-Sn(1)-Cl(1)	92.79(6)
N(2)-Sn(10-N(1)	82.27(9)	N(4)-Sn(1)-N(3)	81.75(10)
N(1)-Sn(1)-N(3)	79.08(8)	C(5)-N(1)-Sn(1)	121.7(2)
C(24)-N(3)-Sn(1)	118.0(2)	C(7)-N(2)-Sn(1)	111.0(2)
C(29)-N(4)-Sn(1)	113.5(2)	N(1)-C(5)-C(6)	118.6(2)
N(3)-C(24)-C(25)	121.1(3)	C(7)-C(6)-C(5)	121.3(2)
C(29)-C(25)-C(24)	117.9(3)	N(2)-C(7)-C(6)	124.3(3)
C(25)-C(29)-N(4)	124.9(3)		

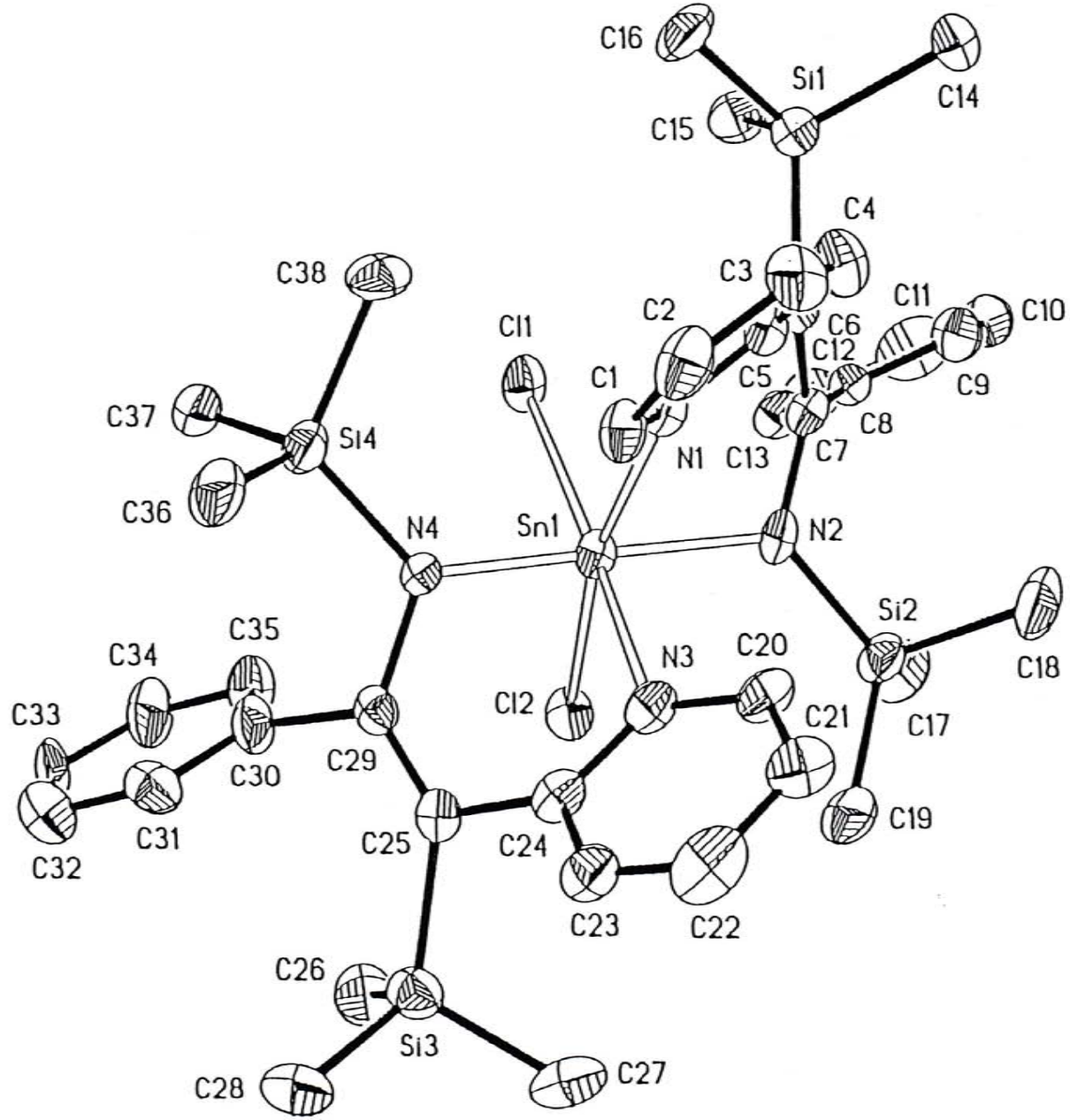


Figure 1. 6 Molecular Structure of $[Sn\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}_2Cl_2]$ (31)

Table 1.10. Comparative selected structural data (av.) for some crystalline isoleptic complexes with amide ligand ($^{-}R^{1}$)

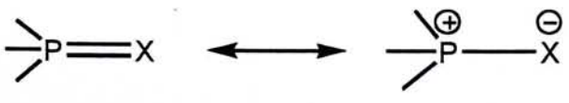
Compounds	*Bond angle, (°)*		*Bond length, (Å)*			
	N-M-N	*C-M-N*	*M-N*	*M-C*	*M-Cl*	*References*
$[Li(R^1)]_2$ **(28)**	----		1.99			33
$[Ge(R^1)(R^{1'})]$ **(29)**	86.30	105.16	2.00	2.04		This work
$[Sn(R^1)]_2$ **(30)**	161.07		2.17			This work
	107.72		2.47			
$[Zr(R^1)]_2Cl_2$ **(32)**	165.00		2.25		2.43	29
$[Sn(R^1)]_2Cl_2$ **(31)**	173.41		2.09		2.42	This work
	82.27		2.28			

Chapter 2 Synthesis and Structures of Group 14 Metal-Chalcogenones

2.1 Multiple bond between group 14 metals and chalcogens

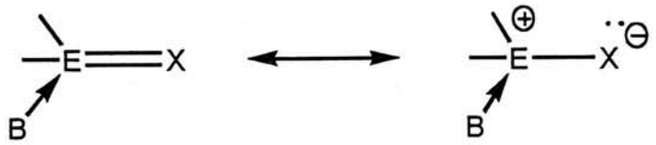
Compounds featuring double bonds between heavier main-group elements were considered to be unstable because of the weak $p\pi$-$p\pi$ bonding. Very little was known for stable metallathiones and metallaselones of heavier group 14 metals such as RR'M=Y (M = Si, Ge, Sn and Pb; Y = S, Se). Some examples of silanethione, silaneselone, and germanethione with intra-molecular coordination from nitrogen atoms are used to stabilize the double bond (thermodynamic stabilization).[1] Tin analogue of thioketones like [^{t}Bu$_2$Sn=S] and [Ph$_2$Sn=S] are known only as transient species, which undergo oligomerization to give the corresponding dimer and trimer, respectively. Compounds containing tin-chalcogen double bond are scarcely found because of the low bond energy (e.g. Sn=S is 31.8 kcalmol^{-1} but C=S, Si=S and Ge=S are 56.1, 46.2 and 40.0 kcalmol^{-1}, respectively).[2] Indeed, sterically unhindered stannanethiones and stannane-selones bearing simple substituents on tin have been known to undergo oligomerization. Therefore, thermally stable compounds containing group 14 metal chalcogens double bond are either base-stabilized or contain a sterically hindered protecting group.[1,3]

Multiple bond with oxygen or sulfur can be found with elements of principle quantum number higher or equal to 3 in which *d*-orbital can be participated in the stabilization or when resonance structures are present so that the metals carry a positive charge and the chalcogen atom a negative charge, a common example is phosphorus (Equation II-1).[4]



(II-1)

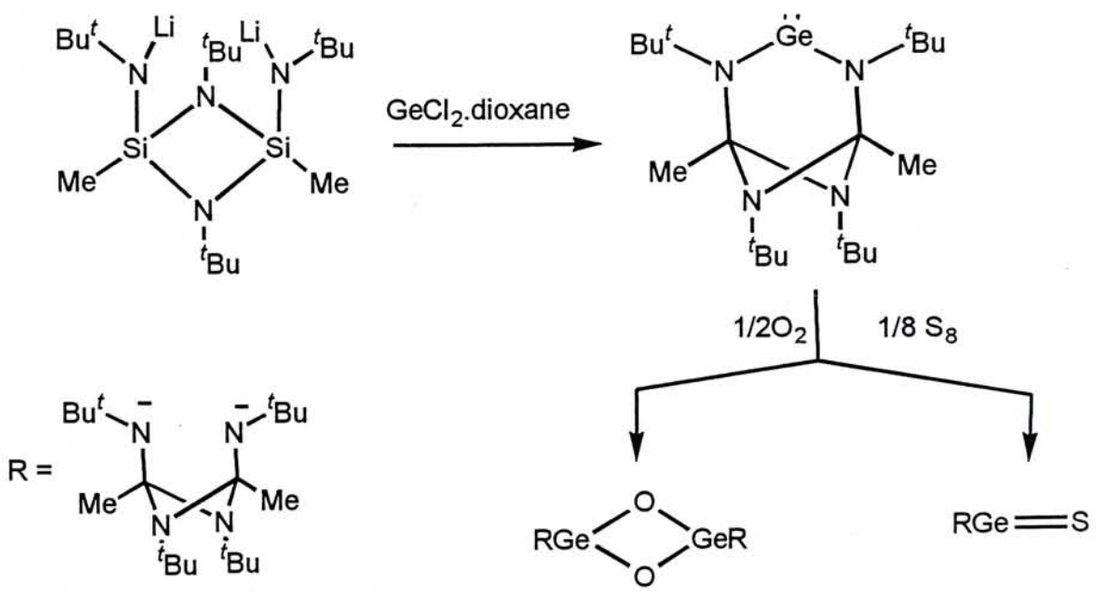
Silicon, germanium and tin-chaclogenides containing intermediate also show this structure (Equation II-2).[5]



(II-2)

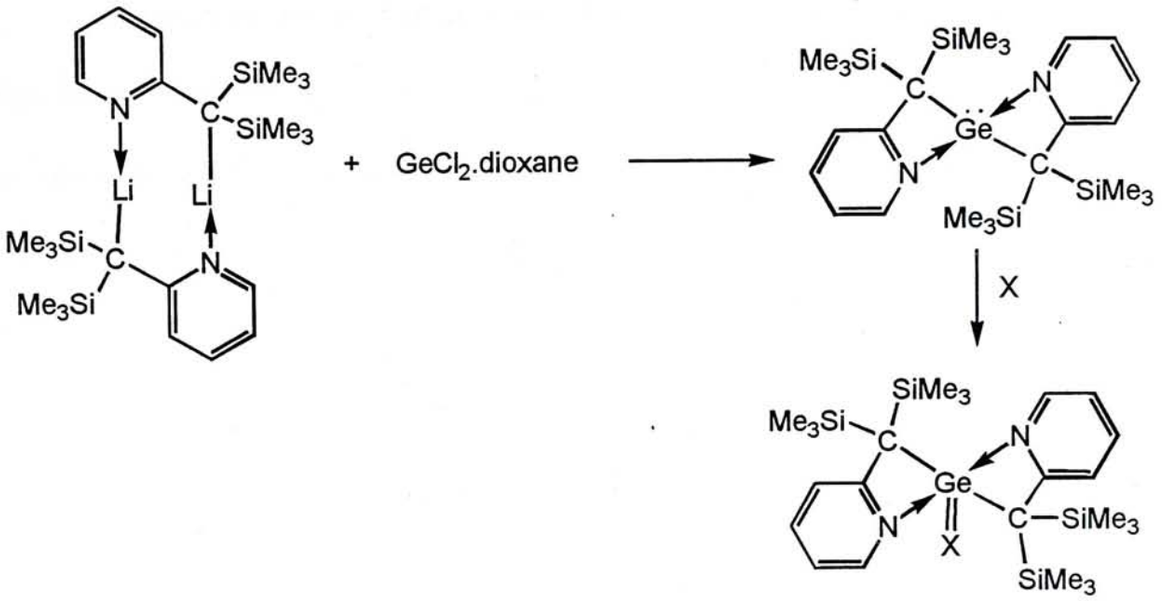
E = Si, Ge
B = Base
X = O, S

Group 14 metal compounds containing a Ge-O single bond and Ge=S double bond can be stabilized by intramolecular coordination of a base. One of the examples is the reaction of polycylic lithium silyamide (Li bridges), with $GeCl_2$.dioxane to give germanium(II) bisamide, which reacts with sulfur or oxygen to form RGe=S [$\bar{R}$ = $(\bar{N}^tBu)_2(MeSi)_2(\bar{N}^tBu)_2$] and the germanium(II) oxygen-bridged dimer $[(MeSi)_2(N^tBu)_4Ge(\mu\text{-}O)]_2$ (**Scheme 2.1**).[6,7]



Scheme 2.1

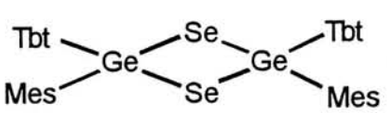
Further examples are compounds **37-39** which have been synthesized by using base stabilized alkyl ligands as shown in **Scheme 2.2**.[8]



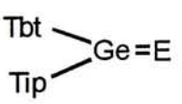
X= S (**37**), Se (**38**), Te (**39**)

Scheme 2.2

Group 14 metal chalcogenides tend to oligomerize readily due to steric reasons. It was found that oligomeization can be avoided by using sterically demanding ligands at the metal center. For examples, [Tbt(Mes)Ge=Se] (**40**) [Tbt = 2,4,6-tris-(bistrimethylsilyl)methyl]phenyl; Mes = 2,4,6-tris(trimethyl)-phenyl][9] and [Tbt(Tip)Ge=E] [E = S **41**, Se **42**; Tip = 2,4,6-triisopropylmethylphenyl] had been reported.[3, 9-11]

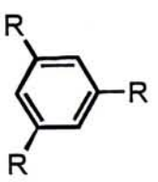


(40)

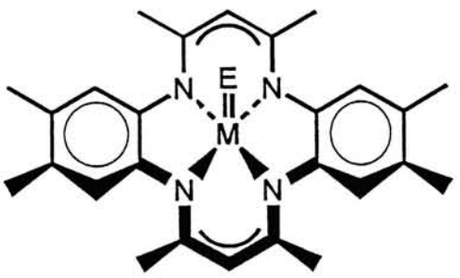


E= S (**41**)
E= Se (**42**)

Tbt: R = $CH(SiMe_3)_2$
Tip: R = $CH(CH_3)_2$
Mes: R = CH_3

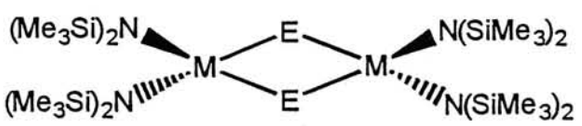


A series of terminal chalcogenido complexes of germanium(IV) and tin(IV) can been stabilized by ligation of the macrocylic octamethyldibenzotetraaza[14] annulene ligand (η^4-Me_8taa). For example, [(η^4-Me_8taa)M=E] [M = Ge; E = S **43**, Se **44**; M = Sn; E = S **45**, Se **46**] have been reported.[12, 13]

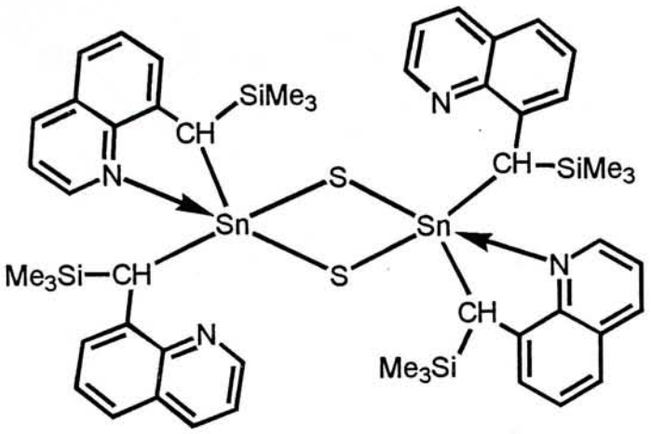


M = Ge, E = S (**43**), Se (**44**)
M = Sn, E = S (**45**), Se (**46**)

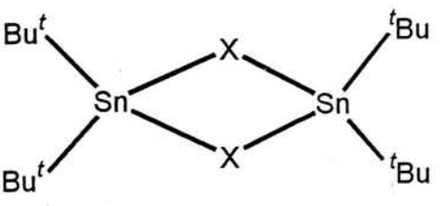
Other examples such as bis[bis(trimethylsilyl)amido]-germanium(IV) and-tin(IV) chalcogenides [{M[N($SiMe_3$)$_2$]$_2$-(μ-E)}]$_2$ (M = Ge, E = S **47**, Se **48**; M = Sn, E = S **49**, Se **50**)[14-16], dialkyltinthiones [{(R^2)Sn(μ-S)}$_2$][17] **(51)** and di-*tert*-butyltin chalcogenides [{^{t}BuSn(μ-X)}$_2$] (X= S **52**, Se **53**, Te **54**) have been reported.[18] These compounds contain a 4-membered (M-E)$_2$ ring bridged dimer.



M = Ge, E = S (**47**), Se (**48**)
M = Sn, E = S (**49**), Se (**50**)

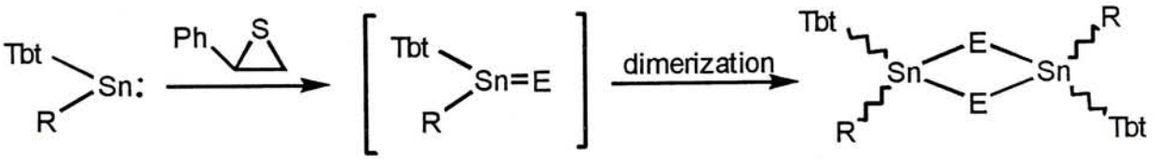


51



X= S (52), Se (53), Te(54)

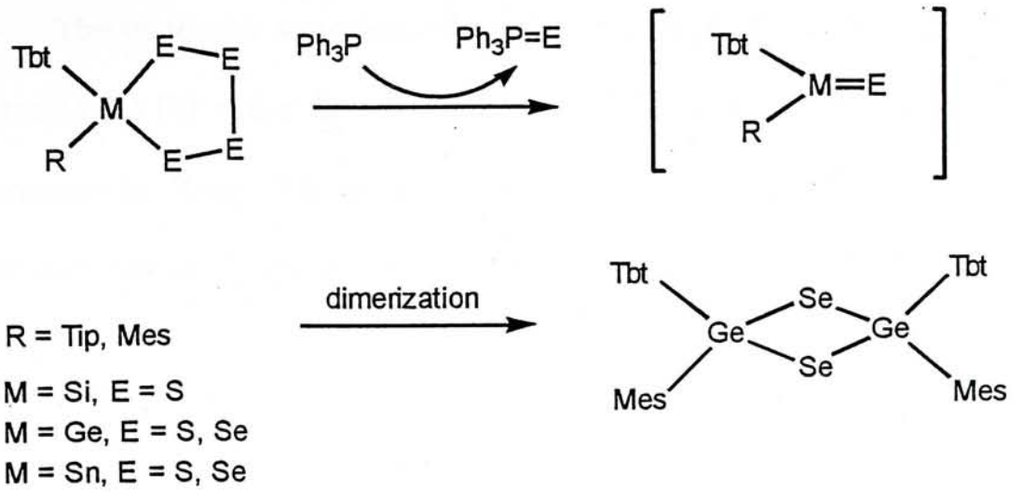
Monomeric diarylstannane-thione and -selone with sterically hindered groups have been detected as intermediates and trapped by various reagents to form cyclo-addition product (**Scheme 2.3**).



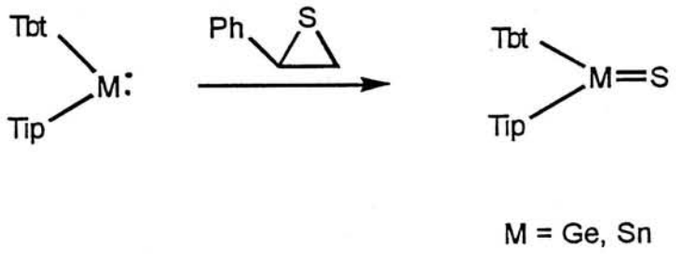
R = Tip, E = S **55**
R = Tip, E = S **56**, Se **57**
R = Mes, E =S **58**

Scheme 2.3

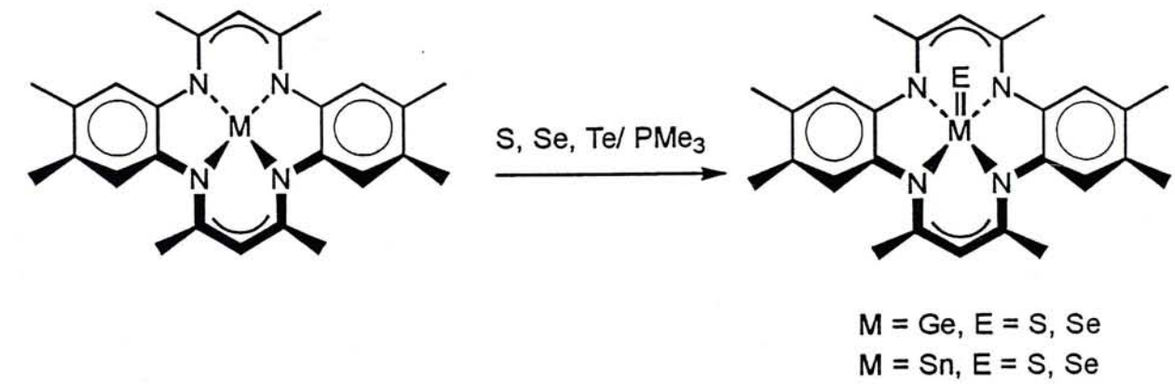
Three synthetic approaches for thioketone analogues had been reported; (i) dechalcogenation of tetrachalcogenametallolanes (R_2MY_4) (M = Si, Ge, Sn; Y = S, Se) (**Scheme 2.4**),[2] (ii) sulfur transfer from styrene episulfide to germylene or stannylenes (**Scheme 2.5**)[10] and (iii) direct chalcogenation of germylene or stannylene by elemental chalcogens (**Scheme 2.6**)[12, 19].

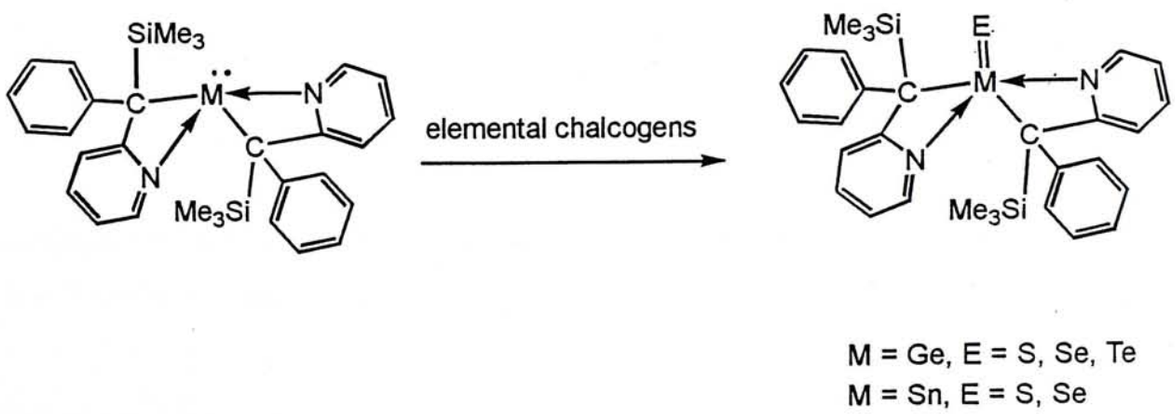


Scheme 2.4



Scheme 2.5





Scheme 2.6

The molecular structures of terminal chalcogenido complexes such as [(η^4-Me_8taa)M=E] [M = Ge; E = S **43**, Se **44**; M = Sn; E = S **45**, Se **46**] have been determined by X-ray diffraction. The nature of the germanium or tin-chalcogene interaction can be represented by two resonance structures (Figure 2.1).[12,13]

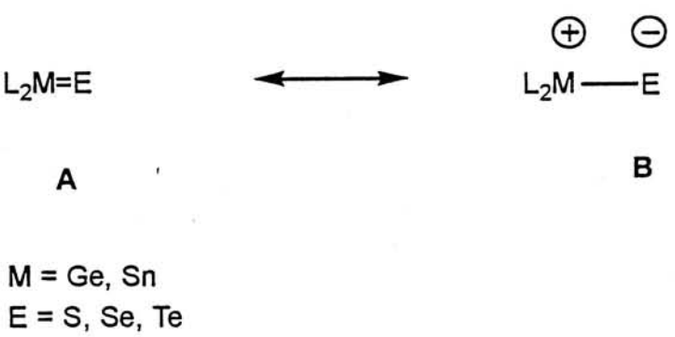


Figure 2.1

In order to address which of the above resonance structures better describe the M-E interaction in the terminal chalcogenido complexes, consideration must be given to the M-E bond lengths (Table 2.1).[20]

Table 2.1. Calculated M-E bond distances (M = Ge, Sn; E = S, Se, Te)

E	$d(Ge\text{-}E)_{calc}$/Å[a]	$d(Sn\text{-}E)_{calc}$/Å[b]	$d(Ge{=}E)_{calc}$/Å[a]	$d(Sn{=}E)_{calc}$/Å[b]
S	2.26	2.44	2.06	2.24
Se	2.39	2.57	2.19	2.37
Te	2.59		2.39	

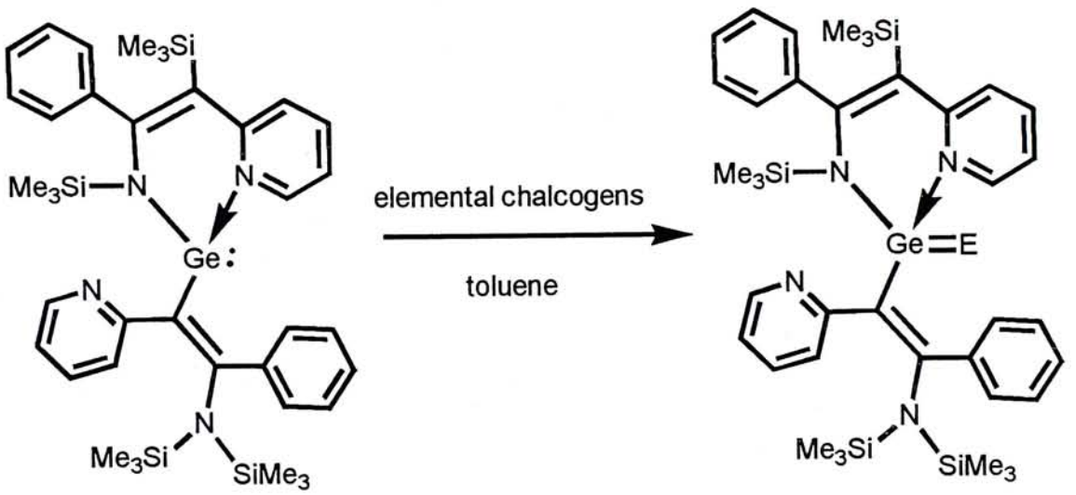
[a] Calculations are based on the sum of single-bond covalent radii of Ge (1.22 Å), Sn(1.40 Å) and (S, 1.04 Å, Se, 1.17 Å and Te, 1.36 Å).

[b] Calculations are based on the sum of the double-bond covalent radii of Ge (1.12 Å), Sn (1.30 Å) and (S, 0.94 Å and Se, 1.07 Å).

2.2 Results and Discussion

2.2.1 Synthesis of germane- and stannane-chalcogenones [$(R^1)(R^{1'})Ge{=}E$], [E = S (59), Se (60)], [$(R^1)_2Sn{=}S$] (61), [$(R^1)(R^{1'})Sn{=}Se$] (62)

The reaction of [$Ge(R^1)(R^{1'})$] (**29**) with stoichiometric amounts of elemental chalcogens in toluene afforded the corresponding thermally stable (alkenyl)amide germane-thione (**59**) and -selone (**60**) in 42% and 62% yield, respectively (**Scheme 2.7**). The reaction proceeded instantaneously at 0 °C, gave yellow crystalline compounds **59** and **60**. These thermally stable chalcogenones were isolated as toluene solvates.



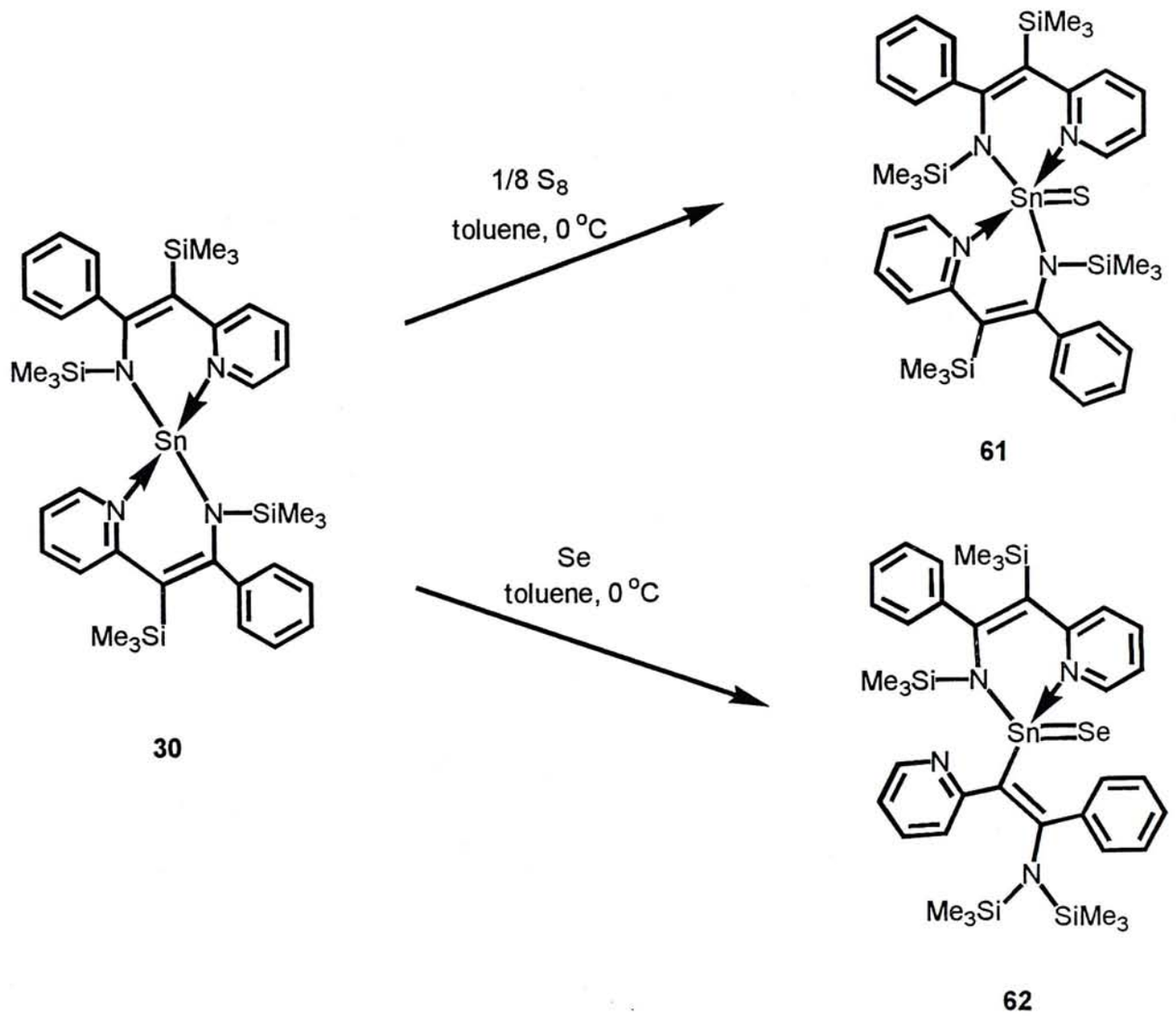
29 E = S **59**, Se **60**

Scheme 2.7

The structural studies have shown that insertion of a chalcogen S or Se to Ge does not change the fundamental ligand skeleton around the metal.

The reaction of [$Sn(R^1)_2$] (**30**) with stoichiomeric amounts of elemental chalcogens in toluene afforded the corresponding thermally stable stannanethione (**61**) and stannanselone (**62**) in good yields (**Scheme 2.8**). Compound **61** was a

terminal sulfido complex. In contrast, the reaction of $[(R^2)_2Sn]$ (**27**) with sulfur gave the sulfur bridged dimer $[(R^2)_2Sn(\mu\text{-}S)]_2$. The reaction of $[(R^1)_2Sn]$ (**30**) with Se gave the stannanselone $[(R^1)(R^{1'})Sn{=}Se]$ (**62**). It is noteworthy that the reaction involved a 1,3-trimethylsilyl shift and rearrangement of one of the amido ligands. This rearrangement of the ligand backbone led to the formation of a new Sn-C bond has been described in section 1.5.1, Equation I-6.



Scheme 2.8

2.2.2 Spectroscopic properties of compounds 59-62

Compounds **59-62** were characterized by microanalysis, mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy. The physical properties for compounds **59-62** are shown in Table 2.2. All the compounds are soluble in THF, ether and toluene but decompose in CH_2Cl_2 and $CHCl_3$. The color ranges of compounds **59-62** vary from pale yellow **59**, to yellow **60** and from pale yellow to yellow in compound **61-62**, indicative of charge transfer from chalcogen to a vacant-metal-centered *d*-orbital (n $\rightarrow \pi^*$ transition)

Table 2.2. Some physical properties for compounds 59-62.

Compounds	*Appearance*	*m.p., °C*[a]	*Yield, %*	*Microanalysis % C, H, N*[b]
$[(R^1)(R^{1'})Ge{=}S]$ (**59**)	Pale yellow	222-226 (dec.)	43	58.07, 7.05, 7.74 (58.22, 6.94, 7.14)
$[(R^1)(R^{1'})Ge{=}Se]$ (**60**)	Yellow	233-236 (dec.)	62	55.00, 6.67, 7.39 (54.94, 6.55, 6.75)
$[(R^1)_2Sn{=}S]$ (**61**)	Pale yellow	246-248 (dec.)	69	57.57, 6.67, 6.60 (56.98, 6.63, 6.41)
$[(R^1)(R^{1'})Sn{=}Se]$ (**62**)	yellow	274-277 (dec.)	88	51.94, 6.32, 6.28 (52.05, 6.21, 6.39)

[a] m.p. were measured in capillary tubes sealed under nitrogen and were uncorrected.

[b] figures in parenthesis are the calculated values based on the molecular formula shown.

Mass spectra of compounds **59** and **62** showed the presence of parent peaks $[M]^+$ at 784 and 877, respectively. While compounds **60** and **61** only showed peaks at 753 and 798 respectively. They were assigned to $[M\text{-}Se]^+$ and $[M\text{-}S]^+$. The mass spectral data for **59-62** are shown in Table 2.3.

Table 2.3. Mass spectra data for compounds 59-62

Compounds	*Parent peak [M]$^+$*	*Other important peaks*
$[(R^1)(R^{1'})Ge{=}S]$ (**59**)	784	753 $[M\text{-}S]^+$, 680 $[M\text{-}S\text{-}R^1]^+$
$[(R^1)(R^{1'})Ge{=}Se]$ (**60**)	----	753 $[M\text{-}Se]^+$
$[(R^1)_2Sn{=}S]$ (**61**)	----	798 $[M\text{-}S]^+$
$[(R^1)(R^{1'})Sn{=}Se]$ (**62**)	877	798 $[M\text{-}Se]^+$

The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data are shown in Table 2.4 and 2.5 respectively. The ^1H NMR spectra of **59**, **60** and **62** displayed signals due to alkenyl and amide ligands which indicate the metals are bonded to different ligands ($\bar{R}^1$) and ($\bar{R}^{1'}$). The $SiMe_3$ groups in compounds **59-60** displayed two signals may be due to overlapping of three $SiMe_3$ groups. The $SiMe_3$ group in the spectra of **61** showed only one peak, it may be due to the overlapping of two different $SiMe_3$ groups. The spectra of **62** displayed four signals at δ -0.02, 0.04, 0.13 and 0.22, due to four different $SiMe_3$ groups. The change in oxidation state from +2 to +4 resulting in the upfield shift of the signals when compared with the parent compounds. The $^{13}C\{^1H\}$ NMR spectra of **59**, **60** and **62** showed two sets of aromatic carbons for the ligand $\bar{R}^1$ and $\bar{R}^{1'}$ whereas **61** showed only one set of the 11 types of aromatic carbon.

Table 2.4. **^{1}H NMR spectral data for compounds 59-62.[a]**

Compounds	*Me_3Si*	*Phenyl*	*Pyridyl*
$(R^1)(R^{1'})Ge{=}S$ (**59**)	0.03, 0.14	6.81 (m), 7.04 (d), 7.12 (t), 7.19 (m)	6.24 (t), 6.84 (br), 6.92 (td), 7.44 (m), 7.81 (d), 8.85 (dd)
$(R^1)(R^{1'})Ge{=}Se$ (**60**)	0.10, 0.21	7.09-7.24 (m), 9.05(d)	6.27 (br), 6.94 (t), 7.06 (d),7.43 (br), 7.92 (br), 9.05 (d)
$(R^1)_2Sn{=}S$ (**61**)	0.04	6.95-7.13 (m)	6.58 (td), 7.35 (d), 7.58 (br), 7.73 (br)
$(R^1)(R^{1'})Sn{=}Se$ (**62**)	-0.02, 0.04, 0.13, 0.22	6.61 (m), 6.89 (d), 6.93 (d), 7.22(d), 8.47 (d)	6.30(d), 6.99(d), 7.11(d), 7.64(d), 8.47(d), 9.23(d)

[a] chemical shifts are in δ (ppm) referenced to internal C_6D_6 (δ 7.15 ppm), 300.13 MHz

Table 2.5. $^{13}C\{^1H\}$ NMR spectral data for compounds 59-62.[a]

Compounds	*Me_3Si*	*$CSiMe_3$*	*Aromatic Carbon*	*PyCM*	*NCPh*
$(R^1)(R^{1'})Ge{=}S$ (**59**)	2.66, 3.06, 3.94	111.68	117.56, 119.81, 120.06, 120.41, 120.74, 123.95, 124.64, 126.04, 126.82, 129.84, 130.06, 130.38, 130.85, 132.01, 135.21, 135.60, 138.72, 139.20, 143.33, 144.14, 144.65, 148.61, 156.56	157.65	161.31, 169.39
$(R^1)(R^{1'})Ge{=}Se$ (**60**)	2.72, 3.13, 4.36	112.44	119.83, 120.77, 13.87, 124.17, 126.90, 126.99, 127.36, 129.28, 129.86, 130.27, 132.14, 135.25, 135.54, 136.70, 138.97, 139.23, 144.25, 144.56, 145.07, 148.28, 156.30, 157.28, 159.89	161.71	168.03, 169.27
$(R^1)_2Sn{=}S$ (**61**)	4.93	113.83	119.00, 124.67, 125.65, 129.29, 130.07, 132.69, 134.46, 137.75, 145.13, 149.11, 159.86		169.46
$(R^1)(R^{1'})Sn{=}Se$ (**62**)	2.15, 3.15, 3.85	119.69	120.51, 124.37, 129.33, 130.40, 131.13, 131.44, 136.87, 138.39, 142.55, 145.32, 146.72, 147.69, 147.91, 158.83	159.49	161.97, 170.49

[a] chemical shifts are in δ (ppm) referenced to internal C_7D_8 (δ 120.00 ppm), 75.47MHz

[b] referenced to internal C_6D_6 (δ 128.00 ppm).

The ^{119}Sn NMR spectroscopic data of compounds **60-62** are shown in Table 2.6. The ^{119}Sn NMR signals lie in the range of δ 188.65 to δ -285.92. These values are quite different from the values of δ 2208 for stannanethione [(Tbt)(Tip)Sn=S],[10] but are comparable to the values of δ -301 and δ -444 for stannanethione and -selone [(η^4-Me_8taa)Sn=E] (X = S, Se), respectively.[13] They are also comparable to the values of δ -100.48 and δ -111.55 for stannanethione and -selone [$(R^2)_2$Sn(μ-S)]$_2$ and [$(R^2)_2$Sn=Se] respectively.[17,19]

Table 2.6. ^{119}Sn NMR Spectroscopic Data for Compound 60-62.

Compounds	*^{119}Sn NMR[a] δ, ppm*
[$(R^1)_2$Sn=S] (**61**)	188.65
[$(R^1)(R^{1'})$Sn=Se] (**62**)	-285.92
[(Tbt)(Tip)Sn=S]	2208
[(η^4-Me_8taa)Sn=E]	-301
[(η^4-Me_8taa)Sn=E]	44
[$(R^2)_2$Sn(μ-S)]$_2$	-100.48
[$(R^2)_2$Sn=Se]	-111.55

[a] recorded in THF/ C_6D_6, referenced to external $SnMe_4$, 149.20 MHz.

2.2.3 Molecular structure of [{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$Sn=S] (61)

Compound **61** crystallizes in the monoclinic $P2_1/n$ (No. 4) space group. The molecular structure of **61** is shown in Figure 2.2. Selected bond distances and angles are shown in Table 2.7. The two amido ligands $\bar{R}^1$ are bond to the central tin atom in a *trans N,N'*-chelating fashion. The angles of N(4)-Sn(1)-N(1), S(1)-Sn(1)-N(3) are 92.49(1)° and 93.98(9)° respectively. The sum of N(4)-Sn(1)-N(2)-S(1) plane is 359.98° which is closely 360° and is nearly perpendicular to the plane of N(1)-Sn(1)-N(3) (171.5(11)°). It can be appropriately described as a distorted trigonal bipyramidal geometry with sulfur atoms occupying the axial position of the pyramidal.

The Sn-S bond distance of 2.29(12) Å is relatively longer than the Sn-S bond distance in [(η^4-Me$_8$taa)Sn=S] (**45**) [2.27(3) Å][16] and shorter than that in the sulfur bridged dimer [(R^2)$_2$Sn(μ-S)]$_2$ (**51**) [2.42(3) Å][17] and [{Sn[N(SiMe$_3$)$_2$]$_2$(μ-S)}$_2$] (**49**) [2.42 Å (av.)].[14] The reduction in bond length is consistent with enhance contribution of π-bonding between Sn and S. For comparison, the calculated values of Sn-S and Sn=S are 2.44 Å and 2.24 Å, respectively.[13,20] The Sn-S bond distance lies between the calculated values of Sn-S single and double bonds. This is an indicative of multiple bond character derived from combination of the resonance structures of **A** and **B** in Figure 2.1. The average Sn-N(pyridyl) bond distance of 2.30 Å and the average covalent Sn-N(amido) bond distance of 2.09 Å are shorter than those values of 2.47 Å and 2.17 Å in the parent compound **30**. The decrease in these distances can be explained by the result of the change in oxidation state from Sn(II) to Sn(IV). The average bond angle of N-Sn-N in the NCCCN skeleton of compound **61** is 82.7°, which is larger than the value of 77.4° in compound **30**.

Table 2.7. Selected bond distances (Å) and angles (°) for compound 61

[{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$Sn=S] (**61**)			
Sn(1)-S(1)	2.291(12)	Sn(1)-N(2)	2.083(3)
Sn(1)-N(4)	2.098(3)	Sn(1)-N(1)	2.296(3)
Sn(1)-N(3)	2.311(3)	N(2)-C(10)	1.403(5)
C(1)-C(6)	1.483(5)	C(6)-C(10)	1.370(5)
C(10)-C(16)	1.506(5)	N(1)-C(1)	1.343(5)
Si(2)-N(2)	1.772(3)	Si(1)-C(6)	1.907(4)
N(2)-Sn(1)-N(4)	112.44(12)	N(2)-Sn(1)-S(1)	123.77(9)
N(4)-Sn(1)-S(1)	123.77(9)	N(2)-Sn(1)-N(1)	84.40(12)
N(4)-Sn(1)-N(1)	92.49(11)	S(1)-Sn(1)-N(1)	94.18(9)
N(2)-Sn(1)-N(3)	93.00(11)	N(4)-Sn(1)-N(3)	81.01(11)
N(1)-Sn(1)-N(3)	171.51(11)	S(1)-Sn(1)-N(3)	93.98(9)
N(1)-C(1)-C(6)	123.20(3)	C(6)-C(10)-N(2)	129.80(3)
C(10)-C(6)-C(1)	119.40(4)	C(10)-C(6)-Si(1)	124.80(3)
C(6)-C(10)-C(16)	115.60(13)		

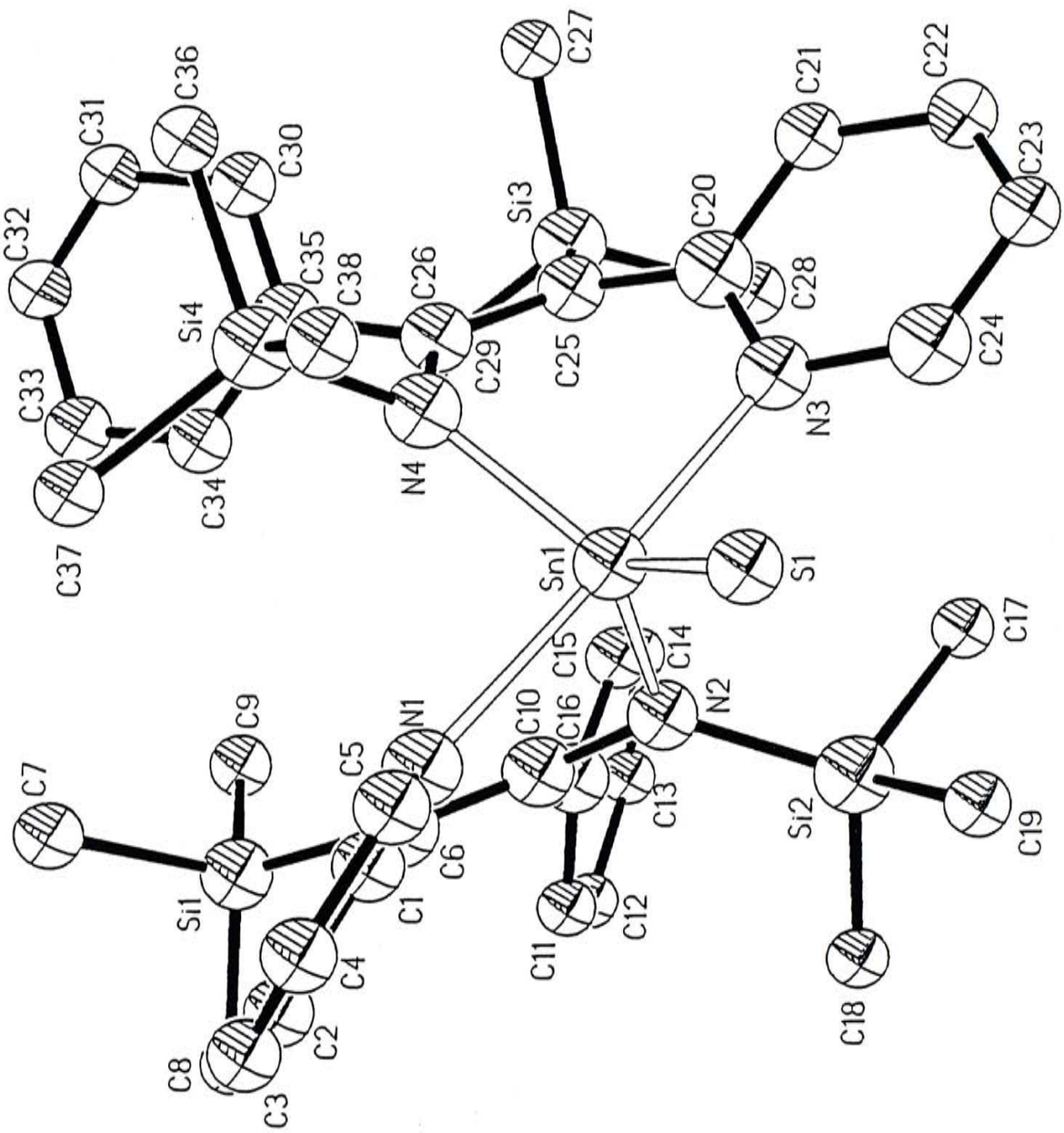


Figure 2.2 Molecular Structure of [{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$Sn=S] (61)

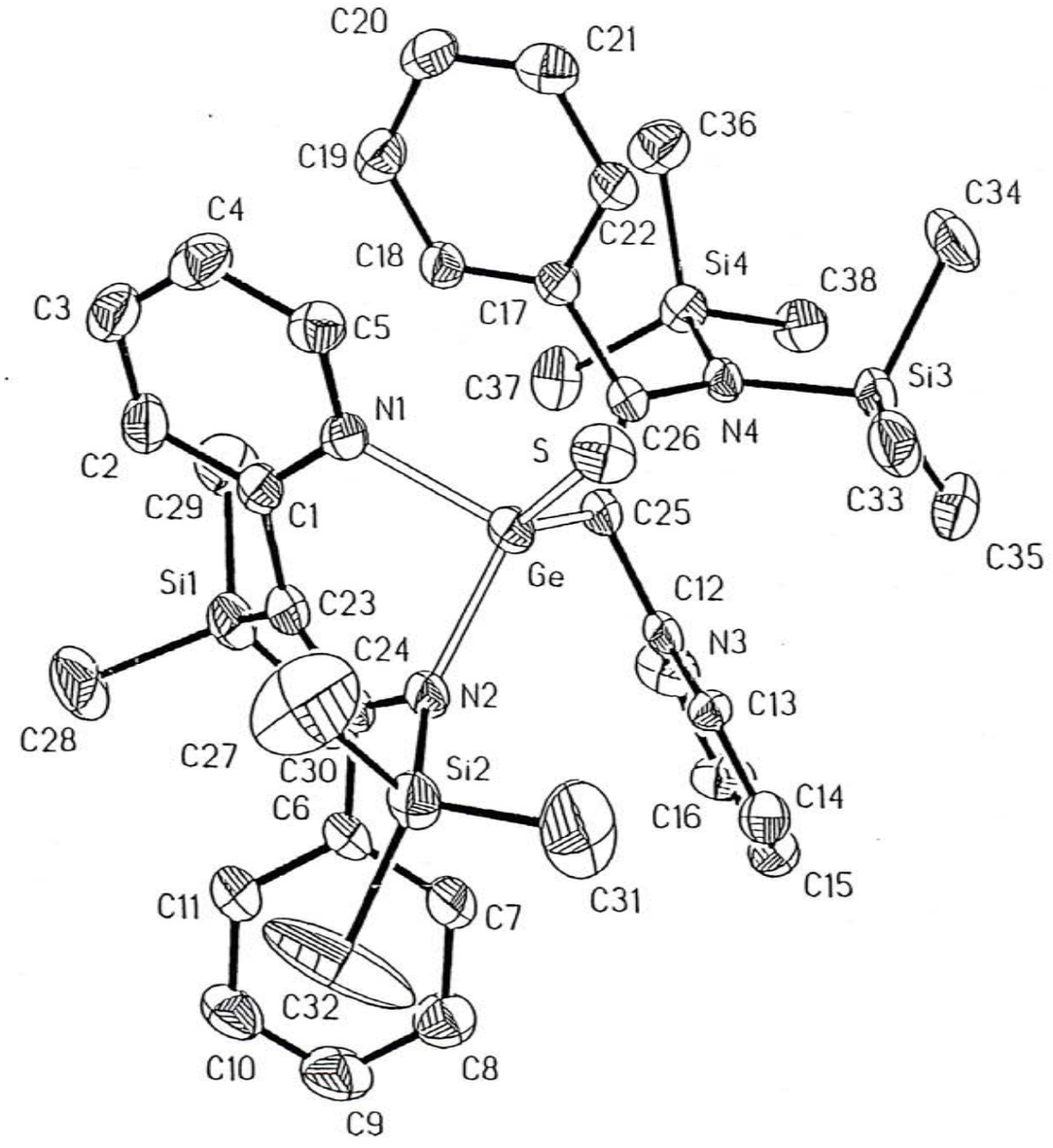


Figure 2. 3 Molecular Structure of [{N(SiMe$_3$)C(Ph)C(C$_5$H$_4$N-2)}{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)$_2$Ge=S] (59)

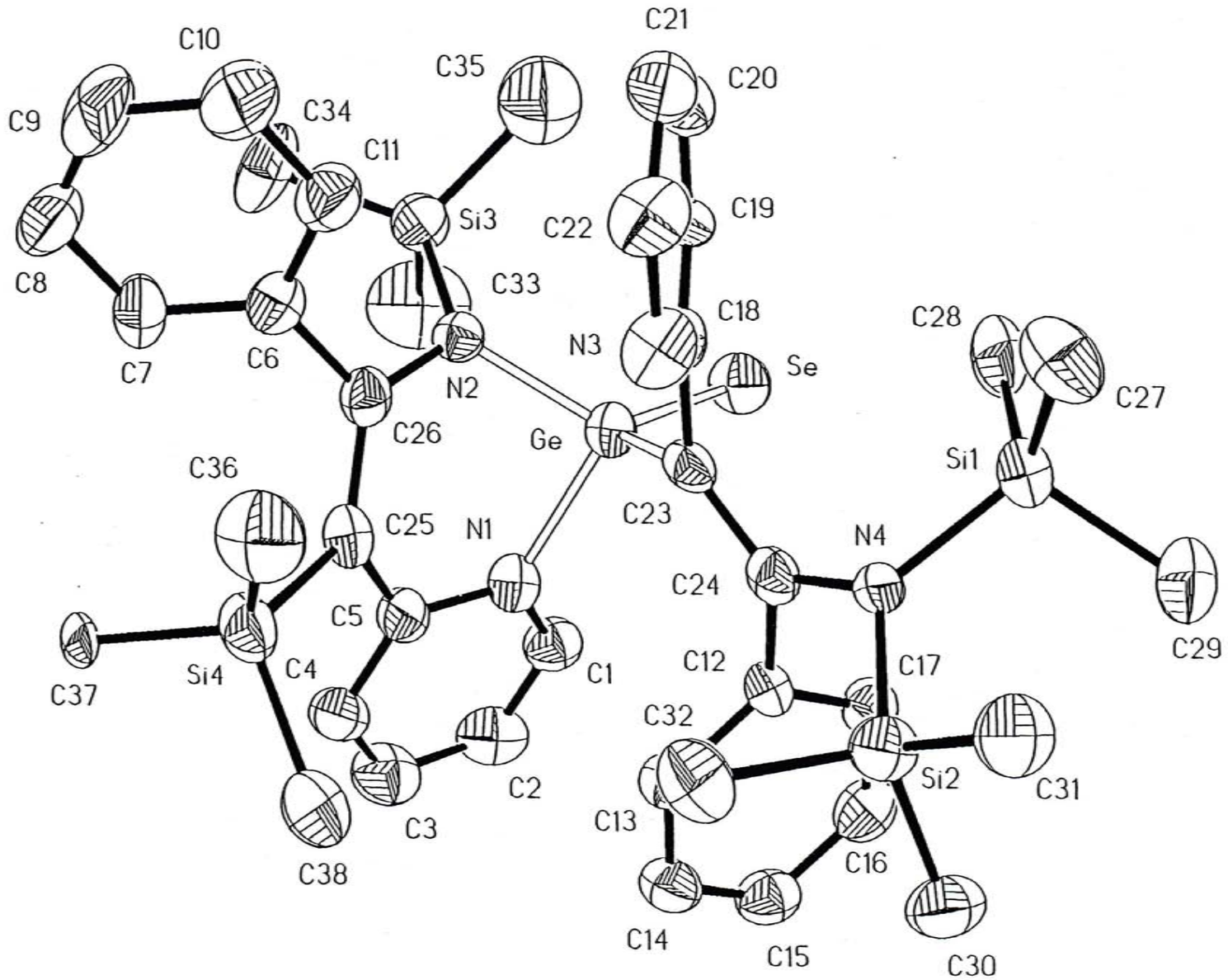


Figure 2. 4. Molecular Structure of [{N(SiMe$_3$)C(Ph)C(C$_5$H$_4$N-2)}{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)$_2$Ge=Se] (60)

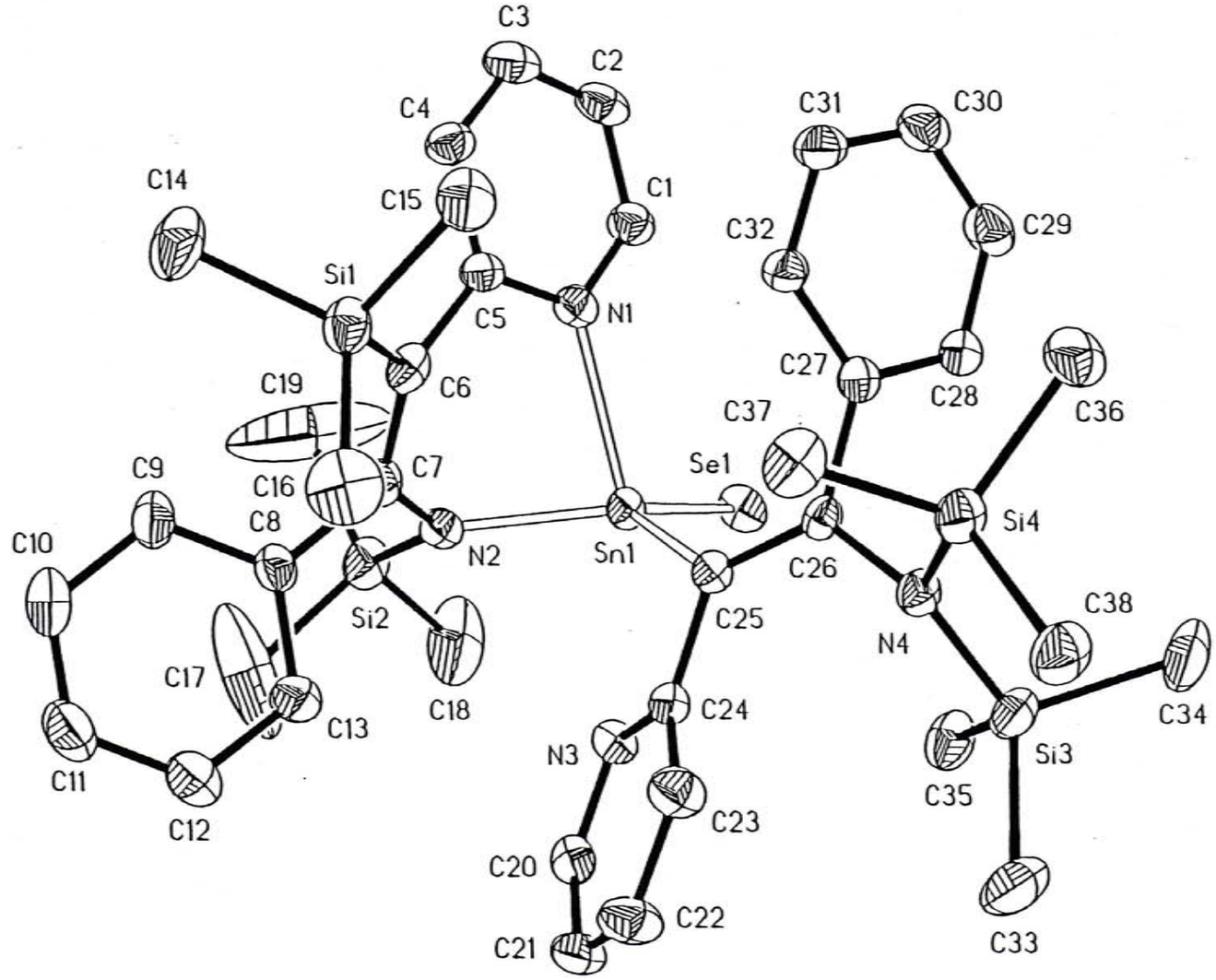


Figure 2. 5 Molecular Structure of [{N(SiMe$_3$)C(Ph)C(C$_5$H$_4$N-2)}{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)$_2$Sn=Se] (62)

2.2.4 Molecular structure of [E=M{C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}{(C_5H_4N-2)C-(Ph)C($SiMe_3$)N($SiMe_3$)}] [(M = Ge, E = S 59, Se 60; M = Sn, E = Se 62]

Compounds **59**, **60** and **62** are isostructural to each other. Compounds **59**, **60** and **62** crystallize in a triclinic $P\bar{1}$ (no.2) space group. The structure of compounds **59**, **60** and **62** with atom numbering schemes are shown in Figure 2.3, 2.4 and 2.5. One of the amido ligand ($\bar{R}^1$) is bonded to the central metal atom in *N,N'*-chelating fashion and the metal center displays a distorted tetrahedral geometry. It is noteworthy that in the structures of compounds **59**, **60** and **62**, one of the ligand is bonded via the alkenyl carbon as a result of rearrangement. The smaller germanium atom allows the 1,3-trimethylsilyl shift in the formation of compound **29**. The rearranged ligand is stable enough even the addition of sulfur and selenium to the central metal coordination sphere. In contrast, with the addition of selenium to the tin compound induced the amido ligand to undergo 1,3-trimethylsilyl shift to form a C-centered ligand. This is presumably a consequence of release in steric congestion at the NCCCN skeletons to accommodate the larger selenium. In the structures of compounds **59**, **60** and **62**, the phenyl group of the ligand is *trans* to the pyridyl ring.

In compound **59**, the Ge-S bond distance of 2.08(8) Å is shorter than the Ge-S distances of 2.11(2) Å in [(η^4-Me_8taa)Ge=S][12] (**43**) and 2.24(1) Å [{C-($SiMe_3$)$_2$$C_5H_4$N-2}$_2$Ge=S][8] (**37**) but longer than the distance of 2.24(1) Å in [(Tbt)(Tip)Ge=S][2,10] (**41**). The Ge-S bond distances in compound **59** can be compared with the calculated distance based on the sum of the relevant single and double bond covalent radii for GeS, (2.26 Å and 2.06 Å) respectively.[20] It suggests that the bonding is appropriately described as intermediate between resonance structure **A** and **B** (Figure 2.1).

In compound **60**, the Ge-Se bond distance of 2.22(9) Å is shorter than the Ge-Se distance of 2.43(2) Å in $[(CPh(SiMe_3)C_5H_4N\text{-}2)_2Ge{=}Se]$[19] (**63**), 2.23(1) Å in $[(\eta^4\text{-}Me_8taa)Ge{=}Se]$[12] (**44**) and 2.25(7) Å in $[\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2Ge{=}Se]$[8] (**38**). The Ge-Se bond distance lies between the calculated values of Ge-Se single (2.39 Å) and double bonds (2.19 Å).

The Ge-C, Ge-N(amido) and Ge-N(pyridyl) distances in compound **59** are 1.97(19), 1.88(17) and 1.99(17) Å and that of **60** are 1.98(4), 1.87(3) and 1.99(3) Å respectively. They are shorter than the bond distances in parent compound **29**. The decrease in these distances is probably due to the increase in oxidation state of Ge from +2 to +4.

In compound **62**, the Sn-Se bond distance of 2.39 Å is slightly longer than the distance of 2.39(1) Å in $[(\eta^4\text{-}Me_8taa)Sn{=}Se]$[13] (**46**) and slightly shorter than the distance of 2.42(1) Å $[(R^2)_2Sn{=}Se]$[17,19] (**64**) and the distance of 2.54 Å (av.) in the bridged dimer $[\{Sn(N(SiMe_3)_2)_2(\mu\text{-}Se)\}]_2$[14-16] (**50**). The Sn-Se bond distance of 2.39 Å in compound **62** is much closer to the sum of the double bond covalent radii of Sn (1.30 Å) and Se (1.07 Å), and the sum of their single bond covalent radii (2.57 Å).[20] Again, this is an indicative of considerable multiple bond character derived from the combination of the resonance structures of **A** and **B**.

The phenyl group of the ligand is *trans* to the pyridyl ring. The Sn-N(pyridyl) and Sn-N(amido) distance are 2.23(2) Å and 2.07(2) Å respectively which are shorter than the average Sn-N bond distances in the parent compound **30**.

The reaction profile of compounds **29** and **30** with elemental chalcogens were found to be different from that of compound **27**. Reaction of compound **29** or **30** with one equivalent of sulfur gave monomeric compounds **59** and **61** respectively. While the reaction of compound **27** with one equivalent of sulfur gave a sulfido-bridged dimer **51**.[17,19] It has been shown by X-ray structures analysis that the

germanium atom in compound **59** was bound to two different ligands, ($\bar{R}^1$) and ($\bar{R}^{1'}$) but compounds $[(R^2)_2Sn(\mu\text{-}S)]_2$ **51** and **61** were tin(IV)-thiones.

Moreover, the reaction of compound **29** and **30** with one equivalent of selenium gave Ge(IV) and Sn(IV) selones. Similar reaction with compounds **60** and **62** gave the compounds which showed one of the amide ligand had undergone 1,3-trimethylsilyl shift. However, compound $[(R^2)_2Sn{=}Se]$ (**64**) showed no rearrangement in the coordinated ligands.[17,19]

Table 2.8. Selected Bond Distances (Å) and Angles (°) for Compound 59.

[S=Ge{C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}{(C_5H_4N-2)C(Ph)C($SiMe_3$)N($SiMe_3$)}] (59)			
Ge-S	2.094(8)	Ge-N(2)	1.878(17)
Ge-N(1)	1.999(17)	Ge-C(25)	1.969(19)
C(25)-C(26)	1.349(3)	N(4)-C(26)	1.435(2)
N(4)-Si(4)	1.768(18)	Si(3)-N(4)	1.764(18)
C(12)-C(25)	1.482(3)	C(17)-C(26)	1.498(3)
N(1)-C(1)	1.357(3)	C(1)-C(23)	1.466(3)
C(23)-C(24)	1.382(3)	N(2)-C(24)	1.388(3)
Si(1)-C(23)	1.902(2)	Si(2)-N(2)	1.778(7)
N(2)-Ge-C(25)	108.47(8)	N(2)-Ge-N(1)	89.01(7)
C(25)-Ge-N(1)	109.14(8)	N(2)-Ge-S	121.21(6)
C(25)-Ge-S	117.76(6)	N(1)-Ge-S	106.85(6)
C(1)-N(1)-Ge	118.8(14)	N(1)-C(1)-C(23)	121.18(18)
C(24)-C(23)-C(1)	124.33(16)	N(4)-C(26)-C(17)	114.34(16)
C(25)-C(26)-N(4)	124.30(18)	C(26)-N(4)-Si(3)	118.97(14)

Table 2.9. Selected Bond Distances (Å) and Angles (°) of Compound 60.

[Se=Ge{C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}{(C_5H_4N-2)C(Ph)C($SiMe_3$)N($SiMe_3$)}] (**60**)			
Ge-Se	2.223(9)	Ge-N(2)	1.873(3)
Ge-N(1)	1.996(3)	Ge-C(23)	1.976(4)
N(2)-C(26)	1.402(6)	C(25)-C(26)	1.399(6)
C(5)-C(25)	1.465(7)	N(1)-C(5)	1.365(6)
C(18)-C(23)	1.502(5)	C(23)-C(24)	1.345(5)
C(12)-C(24)	1.490(6)	N(4)-C(24)	1.441(4)
Si(2)-N(4)	1.757(4)	Si(1)-N(4)	1.767(3)
Si(3)-N(2)	1.762(4)	Si(4)-C(25)	1.894(5)
C(6)-C(26)	1.490(6)		
N(2)-Ge-C(23)	109.71(15)	N(2)-Ge-N(1)	88.87(14)
C(23)-Ge-N(1)	109.02(15)	N(2)-Ge-Se	120.61(1)
C(23)-Ge-Se	116.60(12)	N(1)-Ge-Se	107.97(11)
C(18)-C(23)-Ge	111.4(3)	C(24)-C(23)-C(18)	124.1(3)
C(23)-C(24)-C(12)	120.5(3)	N(4)-C(24)-C(12)	114.9(3)
C(24)-N(4)-Si(1)	118.3(3)	Si(2)-N(4)-Si(1)	122.08(16)
C(24)-C(23)-Ge	122.3(3)	C(26)-N(2)-Ge	113.3(3)
C(26)-N(2)-Si(3)	122.8(2)	Si(3)-N(2)-Ge	121.8(2)
C(25)-C(26)-C(6)	118.54(4)	C(25)-C(26)-N(2)	125.2(4)
C(26)-C(25)-C(5)	117.6(4)	N(1)-C(5)-C(25)	120.6(4)

Table 2.10. Selected Bond Distances (Å) and Angles (°) for Compound 62.

[Se=Sn{C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}{(C_5H_4N-2)C(Ph)C($SiMe_3$)N($SiMe_3$)}] (**62**)			
Sn(1)-Se(1)	2.393(7)	Sn(1)-C(25)	2.165(2)
N(3)-C(24)	1.358(3)	Sn(1)-N(1)	2.230(2)
Sn(1)-N(2)	2.071(2)	C(24)-C(25)	1.451(4)
C(25)-C(26)	1.355(3)	N(4)-C(26)	1.450(3)
Si(4)-N(4)	1.763(2)	Si(3)-N(4)	1.749(2)
N(1)-C(5)	1.344(4)	C(5)-C(6)	1.478(4)
C(6)-C(7)	1.359(4)	N(2)-C(7)	1.403(4)
N(2)-Sn(1)-C(25)	117.73(10)	N(2)-Sn(1)-N(1)	81.69(9)
C(25)-Sn(1)-N(1)	105.49(9)	N(2)-Sn(1)-Se(1)	124.93(7)
C(25)-Sn(1)-Se(1)	118.51(7)	N(1)-Sn(1)-Se(1)	104.36(7)
C(5)-N(1)-Sn(1)	119.5(2)	C(7)-N(2)-Sn(1)	112.8(2)
N(1)-C(5)-C(6)	121.3(2)	C(7)-C(6)-C(5)	119.8(3)
C(6)-C(7)-N(2)	125.8(3)	N(3)-C(24)-C(25)	112.4(2)
C(26)-C(25)-C(24)	127.7(2)	C(24)-C(25)-Sn(1)	103.3(2)
C(25)-C(26)-N(4)	123.1(2)	C(26)-C(25)-Sn(1)	123.4(2)
C(25)-C(26)-C(27)	121.1(2)	N(4)-C(26)-C(27)	115.7(2)

Table 2.11. Structural data of some germane-thiones.

Compounds	*Ge-S (Å)*
$[(R^1)(R^{1'})Ge{=}S]$ (**59**)	2.08(8)
$[(\eta^4\text{-}Me_8taa)Ge{=}S]$ (**43**)	2.11(2)
$[\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2Ge{=}S]$ (**37**)	2.24(1)
[(Tbt)(Tip)Ge=S] (**41**)	2.24(1)

Table 2.12. Structural data of some germane-selones.

Compounds	*Ge-Se (Å)*
$[(R^1)(R^{1'})Ge{=}Se]$ (**60**)	2.22(9)
$[(CPh(SiMe_3)C_5H_4N\text{-}2)_2Ge{=}Se]$ (**63**)	2.43(2)
$[(\eta^4\text{-}Me_8taa)Ge{=}Se]$ (**44**)	2.25(1)
$[\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2Ge{=}Se]$ (**38**)	2.25(7)

Table 2.13. Structural data of some stannane-thiones.

Compounds	*Sn-S (Å)*
$[(R^1)_2Sn{=}S]$ (**59**)	2.29(12)
$[(\eta^4\text{-}Me_8taa)Sn{=}S]$ (**45**)	2.27(3)
$[(R^2)_2Sn(\mu\text{-}S)]_2$ (**51**)	2.42(3)
$[\{Sn\{N(SiMe_3)_2\}_2(\mu\text{-}S)\}_2]$ (**49**)	2.42 (av.)

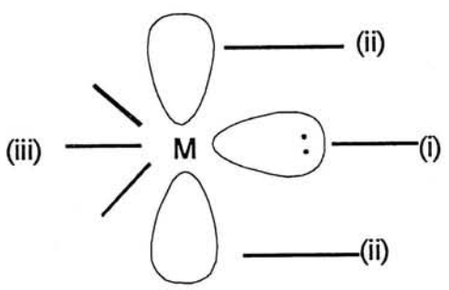
Table 2.14. Structural data of some stannane-selones.

Compounds	*Sn-Se (Å)*
$[(R^1)(R^{1'})Sn{=}Se]$ (**62**)	2.39(7)
$[(\eta^4\text{-}Me_8taa)SnSe]$ (**46**)	2.39(1)
$[(R^2)_2SnSe]$ (**64**)	2.42(1)
$[\{Sn[N(SiMe_3)_2]_2(\mu\text{-}Se)\}_2]$ (**50**)	2.54 (av.)

Chapter 3 Reactivities of Low-valent Group 14 Organometallics Compounds

3.1 Introduction

Bivalent group 14 metal alkyls, MR_2 (M = Ge, Sn, Pb) are usually more reactive than their tetra-valent compounds by virtue of the stereoactive lone pairs electrons. The structure of some monomeric group 14 compounds both in solid and gaseous state have been studied by X-ray crystallography and electron diffraction. Dialkyl stannylene $[Sn(Bsi)_2]$ [Bsi = $CH(SiMe_3)_2$] (**2**) had been studied extensively by Lappert and coworkers.[1] They have shown that $[Sn(Bsi)_2]$ (**2**) can behave as (i) a Lewis base, (ii) a Lewis acid, or (iii) it can undergo oxidative addition (insertion reactions). Different reactive centers in Group 14 carbene analogues are shown in Figure 3.1



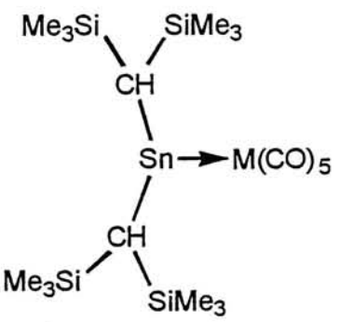
(i) act as Lewis acid
(ii) act as Lewis acid
(iii) the low-valent unsaturated Group 14 metal atom

Figure 3.1 A diagram of different reactive centers in group 14 carbene analogues

3.1.1 Lewis base behavior

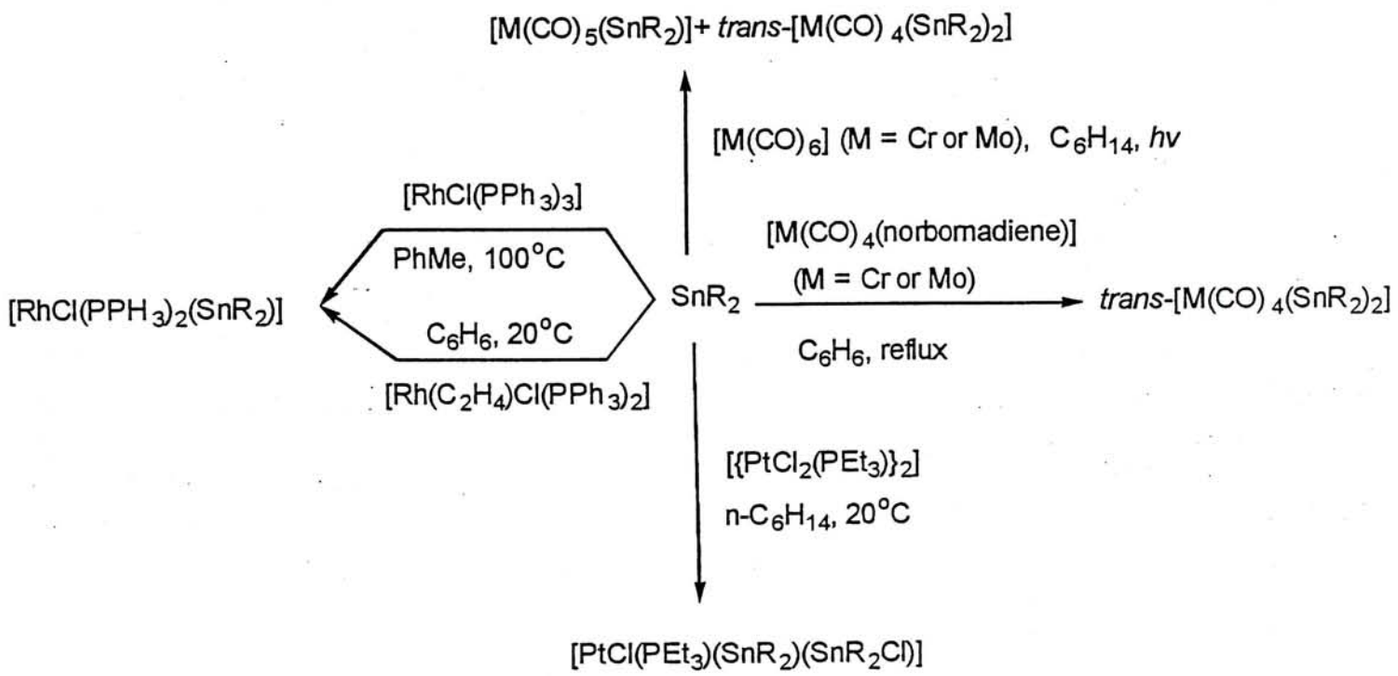
Neutral donors can be classified by whether the ligating atom is carbon (e.g., RNC, or nuclephilic carbene) or element taken from Group 15 or 16 (e.g. NH_3, PPh_3, or SEt_3). It can extend the range of donors to include the heavy elements of Group 14.

For dialkylstannylenes, there have been a few reports concerning the synthesis and characterization of transition metal-stannylene complexes including both base-stabilized and base free.[2-4] The stannylene-transition metal complex was obtained by UV irradiation of $Sn[CH(SiMe_3)_2]_2$ and $[M(CO)_6]$ [M = Cr, Mo] in hexane solution gave moderate yield of the stannylene-transition metal complexes, $[M(CO)_5Sn(Bsi)]$ [M = Cr (**65**), Mo (**66**)], formed by displacement of one molecule of carbon monoxide.



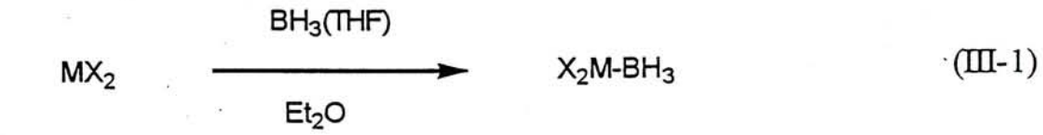
M = Cr (**65**), Mo (**66**)

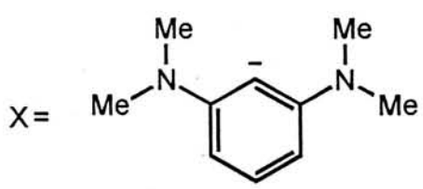
Reactions between Lewis base and corresponding hexacarbonyls frequently lead to more than one carbonyls group being substituted and small amount of *trans*-disubstituted compounds.[5] Some reactions of SnR_2 are summarized in **Scheme 3.1**.



Scheme 3.1 Lewis –base reactions of SnR_2 [R = $CH(SiMe_3)_2$]

Diarylstannylene and -germylene, $[M\{C_6H_3(NMe_2)_2\text{-}1, 2\}_2]$ (M = Ge (**67**), Sn (**68**)) react with Lewis acid such as BH_3 to form monomeric adducts of a intramolecularly base-stabilized complex of the type $[X_2M\rightarrow BH_3]$ [M = Ge (**69**), Sn (**70**); $\bar{X} = \bar{C}_6H_3(NMe_2)_2\text{-}1, 2$] as shown in Equation III-1.[6]





Similar reaction between $[Sn(Bsi)_2]$ and BF_3 was found to be unsuccessful. The reaction with BCl_3, in 1:1 stoichiometric ratio occurred in hexane solution below -30 °C and gave a white precipitate of impure $[(Bsi)_2SnCl_2]$. Recently, a donor-acceptor complex $[(R^2)_2Sn\rightarrow SnCl_2]$ (**71**) had been isolated by the reaction of $[Sn\{CH(SiMe_3)(C_9H_6N\text{-}8)\}_2]$ (**27**) and $SnCl_2$. Compound **71** can undergo ligand-halogen exchange to form another intermediate compound, $[(R^2)SnCl]$ (**72**), which can proceed further to $[Sn(R^2)_2Cl_2]$ (**88**) at higher temperate via transition state **A**.[7,8]

Sily-, stannyl- and plumbyl-silver(I) and copper(I) compounds are stabilized by using chelating and monodentate phosphine ligands. They were prepared from the procedures in Equations III-2 and III-3 under controlled conditions without competing CuSn bond cleavage.[9,10]

$$CuX(PMe_3)_3 + SnCl_2 \longrightarrow Cu(SnXCl_2)(PMe_3)_3 \qquad \text{(III-2)}$$

X=Cl (**73**)
X= I (**74**)

$$Ag(PPh_3)_3Cl + SnCl_2 \xrightarrow{CH_2Cl_2} Ag(PPh_3)_3SnCl_3 \qquad \text{(III-3)}$$

(**75**)

Compounds such as $[\{(C_6H_5)_3P\}_3MSnCl_3]$ (M = Cu (**76**), Ag (**77**), Au (**78**)) have been prepared. It was used to study the bascity of $SnCl_3^-$ and to examine the effect of the electron withdrawing ability of Lewis acids by the $SnCl_3$ stretching frequencies which are shown in Table 3.1.

Table 3.1. $SnCl_3$ stretching frequencies

Compounds	ν_{symm} cm^{-1}	ν_{asymm} cm^{-1}
$[(C_6H_5)_4P)_3CuSnCl_3]$	315	288
$[(C_6H_5)_4P)_3AgSnCl_3]$	313	288
$[(C_6H_5)_4P)_3AuSnCl_3]$	309	286

From the above data, most of the compounds contain a tin(II)-M'(I) bond (M' = Cu, Ag and Au). The coordination structures of these compounds are probably due to $d\pi$-$d\pi$ bonding between the central metal, the phosphorus and tin so that the buildup of electron density on the metal can be avoided. From the infrared data given in Table 3.1, it can be seen that the $SnCl_3$ stretching frequencies increase upon coordination to a Lewis acid.[11]

3.1.2 Lewis-acid behavior

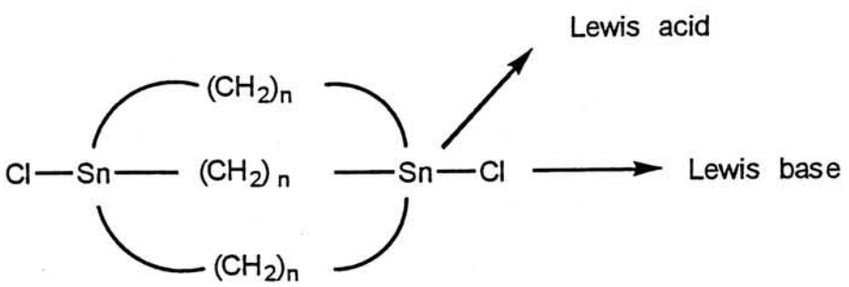
Base-stabilized complexes, $[(CO)_5CrMR_2.base]$[2-4] and $[(CO)_4FeMR_2.base]$, had been reported. The stability of these complexes depend on the base strength. For example in the iron complex, the stability follows the sequence: pyridine> acetone> tetrahydrofuran> diethyl ether. Attempts to remove the base molecule from the complex had led to decomposition. The three-coordinate stannylene-transition metal complexes might only be isoable if the groups attached to tin possess a capacity for interaction with the vacant *p* orbital, to give rise to an 'internal-stabilization' effect similar to that operative in most carbene metal complexes.

Lappert's work demonstrated that neither the ligating base nor internal stabilization was a necessary requirement if the alkyl group was very large. Mark's work suggested that empty *p* orbital in the complex might still possess some Lewis

acidity.[1]

The coordinated divalent group 14 metal and metalloid species can behave simultaneously as strong, coordinatively unsaturated Lewis acids and strong Lewis bases.[4] The lack of reaction between $[(CO)_5MoSn(Bsi)_2]$ and triphenyl phosphine in refluxing benzene provided a qualitative indication of the relative donor strength of the two ligands and also it was a further indication in such complexes. In general, these evidences suggested that the Lewis acidity of the free molecules of $[Sn(Bsi)_2]$ (**2**) might be low.[1]

Tin macrocycles can act as Lewis Acidic hosts like [1,10-dichloro-1,10-dostammabiclo [8.8.8] hexacosane] and benzyltriphenylphosphonium chloride (**79**). Compound **79** is a stannate-stannane species wherein one of the Lewis acidic tin bonds the chloride strongly and other interacts weakly. The crystalline complexes contain halide ion bound within a marcopolycyclic host in which are held by dative, Lewis-acid-base bond.[12]

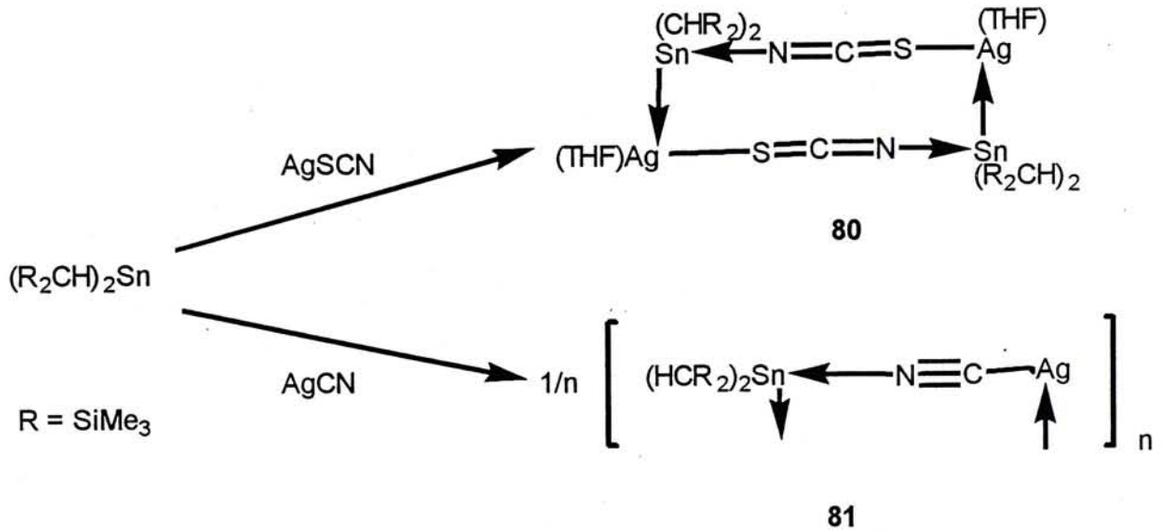


n = 6, 8, 10, 12

(79)

The reaction of $[Sn(Bsi)_2]$ [Bsi = $CH(SiMe_3)_2$] with Ag(I) compound yielded the heterobimetallic Sn-Ag complex $[Ag(SCN)\{Sn(Bsi)_2\}\text{-}(thf)_2]$ (**80**) and $[(1/n)(AgCN)\{Sn(Bsi)_2\}_n]$ (**81**). These two complexes are centrosynmetric dimers

comprising a central SnNCSAgSnNCSAg macrocycle. They can acts as both Lewis acid and Lewis base simultaneously **(Scheme 3.2)**.



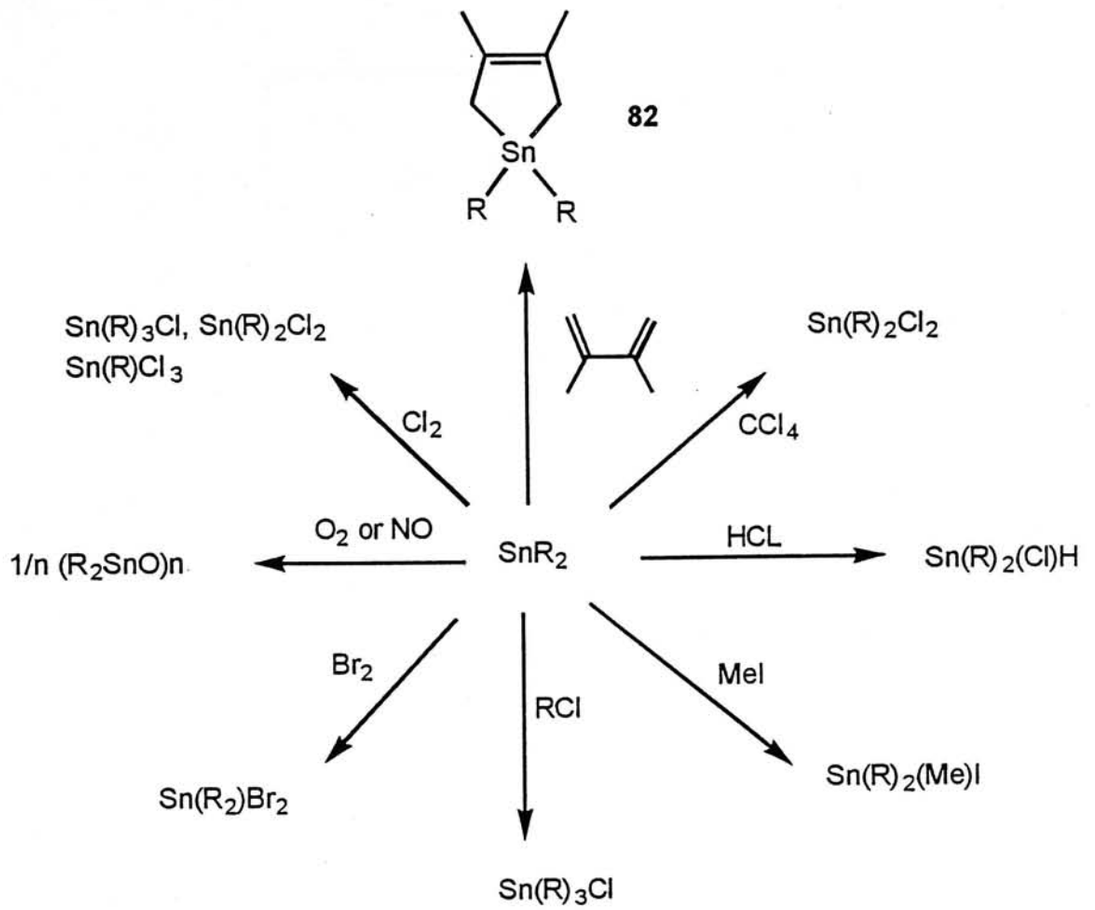
Scheme 3.2

They act as Lewis acid due to the vacant *p*-orbital which accepts electron donating from nitrogen in SCN and act as Lewis base by donating the lone pair electron to the Ag atom.[13]

3.1.3 Oxidative-addition (or insertion) reaction

Oxidative addition reactions of dialkylstannylenes with various reagents AB (small molecules) to yield the metal(IV) adducts had been studied extensively by Lappert and coworkers.[1] Some of oxidative addition reaction of $[Sn(Bsi)_2]$ (**2**) are summarized in **Scheme 3.3**.

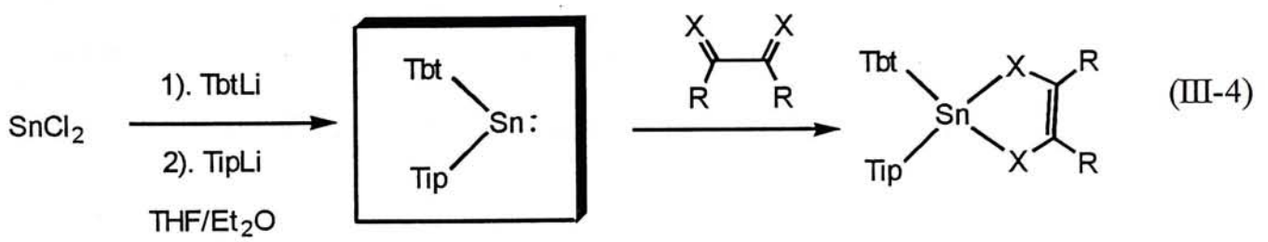
Hydrogen chloride in diethyl ether reacts rapidly with $[Sn(Bsi)_2]$ (**2**) at room temperature to form $[Sn(Bsi)_2(Cl)H]$ as a white solid. The ^1H NMR spectrum showed two equivalent peaks in the region of the $SiMe_3$ protons. All the compounds $[Sn(Bsi)_2(X)Y]$ showed a doublet $SiMe_3$ ^1H NMR signal which is attributed to the prochiral tin atom.



Scheme 3.3 Oxidative addition (or insertion) of SnR_2 [$\bar{R} = \bar{C}H(SiMe_3)_2$] (**2**)

Group 14 carbene analogues often undergo oxidative-addition reaction to conjugate dienes or acetylenes. Trapping reactions are also used in identifying thermally unstable dialkylgermylenes and -stannylene.[14-18] For example, GeI_2 reacts with buta-1,3-diene and its substituted derivatives to give the metallacyclic products of 1,3-addition and with but-2-yne to yield [{MeC=CMeGeI$_2$}$_2$].[19] The reaction of [Sn(Bsi)$_2$] (**2**) with 2,3-dimethylbuta-1,3-diene gave a [1+4]cycloadduct of **82** (**Scheme 3.3**) but there was no detectable reaction with either tetraphenylbuta-1,3-diene or diphenylacetylene. Dialkylstannylenes were also reported to react with benzil and 3,5-di-*tert*-butylbenzoquinone to yield [4+1]cyclcoadduct of **83b** and **84**

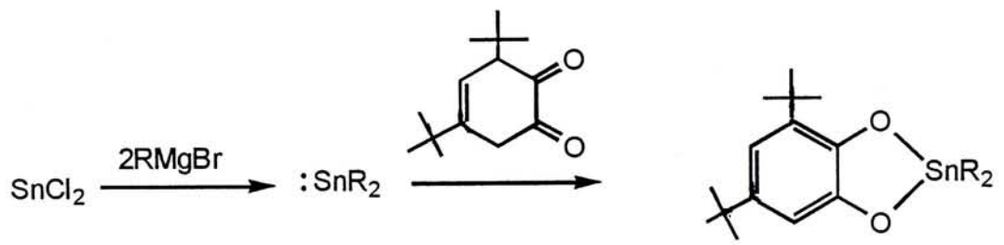
respectively (Equation III-4 and III-5).[17,20]



(III-4)

83a (R = Me, X = CH_2)

83b (R = Ph, X=O)



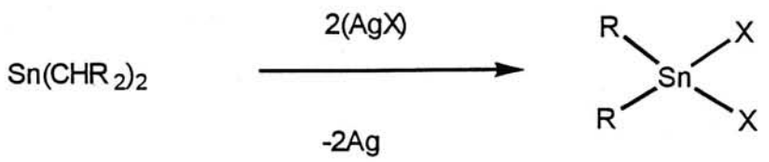
(III-5)

R = 2, 4, 6-(Pr^i)$_3C_6H_2$

84

It is noteworthy that group 14 carbene analogues also react with group 16 element to form some reactive thioketone analogues which contain double bonds between group 14 and 16 elements.

Recently, an oxidative addition adduct of $[Sn(Bsi)_2X_2]$ (X = NCO (**85**), I (**86**)) have been synthesized by Lappert and coworkers (Equation III-6).[13]



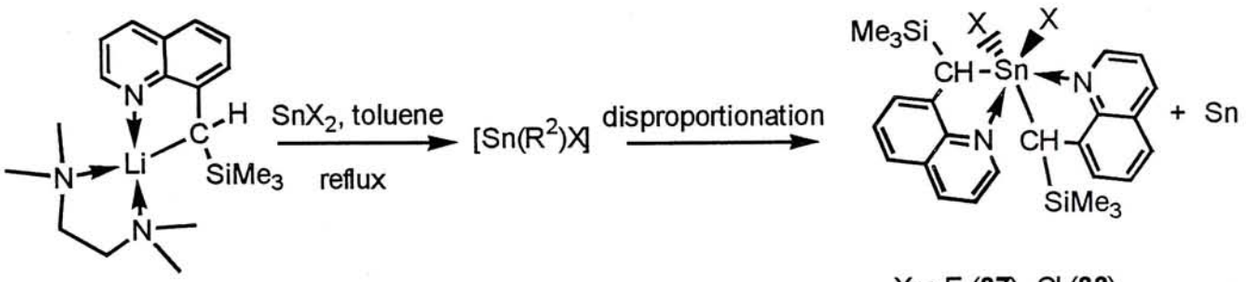
(III-6)

R = $CH(SiMe_3)_2$

X = NCO (**85**)

I (**86**)

The reaction of $[Sn(R^2)_2]$ [$\bar{R}$ = $\bar{C}H(SiMe_3)C_9H_6N$-8] (**27**) with MeI in toluene to yield $[(R^2)_2SnMe(I)]$ had been carried out by our coworker.[8] Synthesis of dialkyltin dihalides $[Sn(R^2)_2X_2]$ (X = F, Cl, Br, I) had also been carried out by our group.[7,8] The reaction was proposed to proceed *via* the monoalkyl-halidostannylene $[Sn(R^2)X]$ as the intermediate, which was presumably unstable at refluxing temperature and underwent a disproportionation reaction immediately to give $[Sn(R^2)_2X_2]$ and tin metal (**Scheme 3.4**). The reaction mechanism may involve the transition state **A** (Figure 3.2) which proceeds to $[Sn(R^2)_2X_2]$ at higher temperature.



X = F (**87**), Cl (**88**),
Br (**89**), I (**90**)

Scheme 3.4

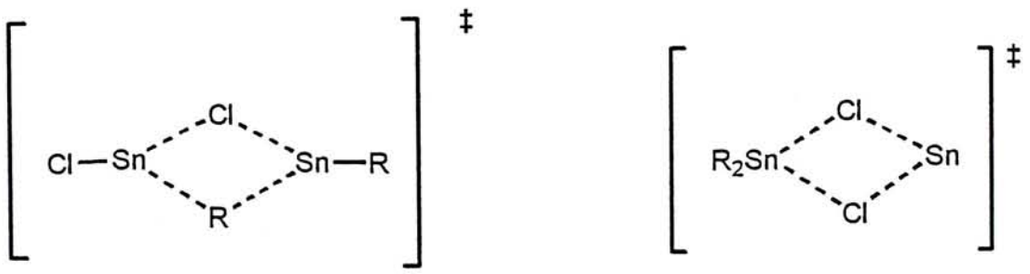
Halogens are known to undergo oxidative-addition reactions with dialkylstannylenes to form dialkyltin dihalides, for example, $[Sn(Bsi)_2Br_2]$[1] and $[Sn\{(CH_2NMe_2)C_6H_3\text{-}2,6\}\{(CH_3)C_6H_4\text{-}4\}\}I_2]$ are the products of halogenation.[21]

3.2. Results and Discussions

3.2.1. Lewis acid-base behavior of $[Sn(R^2)_2]$

3.2.1.1 Reaction of $[Sn(R^2)_2]$ (27) with group 11 metal derivatives (M = Ag, X = Cl (91), I (92), SCN (93), CN (94); M = Cu, X = Cl (95), I (96)) - Synthesis of $[Sn(R^2)_2 \rightarrow (\mu\text{-}AgCl)]_2$

The redistribution reaction of $SnCl_2$ with homoleptic dialkylstannylene $[Sn(Bsi)_2]$ (**2**) leading to $[Sn(Bsi)_2Cl_2]$ and Sn or to $(RSnCl)_n$ [$\bar{R} = \bar{C}(SiMe_3)_2C_5H_4N$-2, n = 1 or $R = \bar{N}(SiMe_3)_2$, n = 2], had been reported by Lappert and coworkers.[22, 23] The reaction mechanism was proposed to involve transition state **A** for $\bar{R}$ capable of functioning in a bridging mode, such as $[\bar{C}(SiMe_3)_2C_5H_4N$-2] and transition state **B** if $\bar{R}$ was a nonfunctioning ligand such as $[\bar{C}H(SiMe_3)_2]$ (Figure 3.2).



A **B**

Figure 3.2

Reaction between group 11 metal derivatives AgX (X = Cl (**91**), I (**92**), SCN (**93**), CN (**94**)) under room temperature and with CuX (X = Cl (**95**), I (**96**)) under 0 °C had been carried out in this work. The product $[Sn(R^2)_2 \rightarrow (\mu\text{-}AgCl)]_2$ (**91**) obtained was a donor-acceptor type complexes. It is proposed that the complex is a halogenated agent and is a preliminary intermediate to the chloro-bridging of the oxidative-addition reaction. The complex may then undergo further metal-halogen

exchange to form another intermediate compound [Sn(R^2)X], which may proceed to [Sn(R^2)$_2$Cl$_2$] at higher temperature using excess AgCl under refluxing condition via transition state **A**. (**Scheme 3.5**).

The vacant orbitals are conceivably occupied by the nitrogen lone pairs from the quinolyl ligands. Hence, [Sn(R^2)$_2$] behave as a Lewis base and favors formation of a donor-acceptor type complex by donating a lone pair from its sp^2 orbital to the vacant *pz* orbital of the Lewis acid AgCl. On the basis of the structural data, compound **91** is best described as a donor-acceptor complex with a single bond between Sn and Ag.

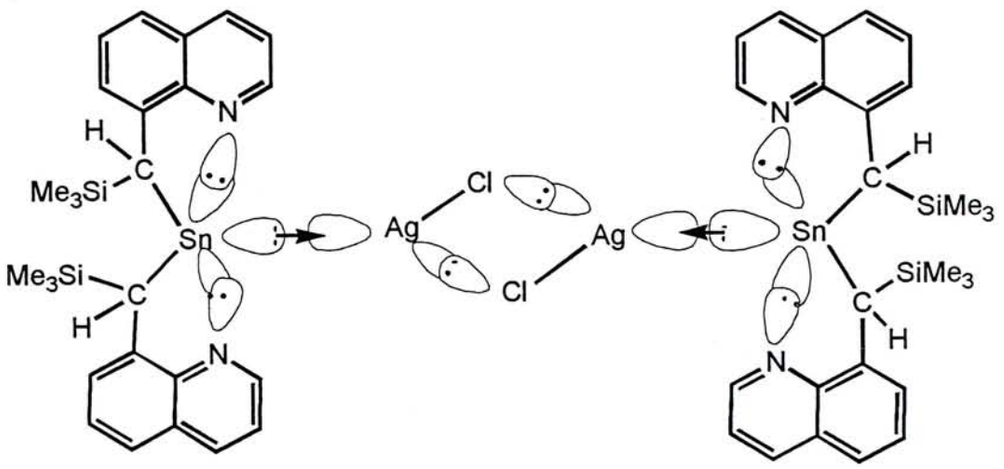
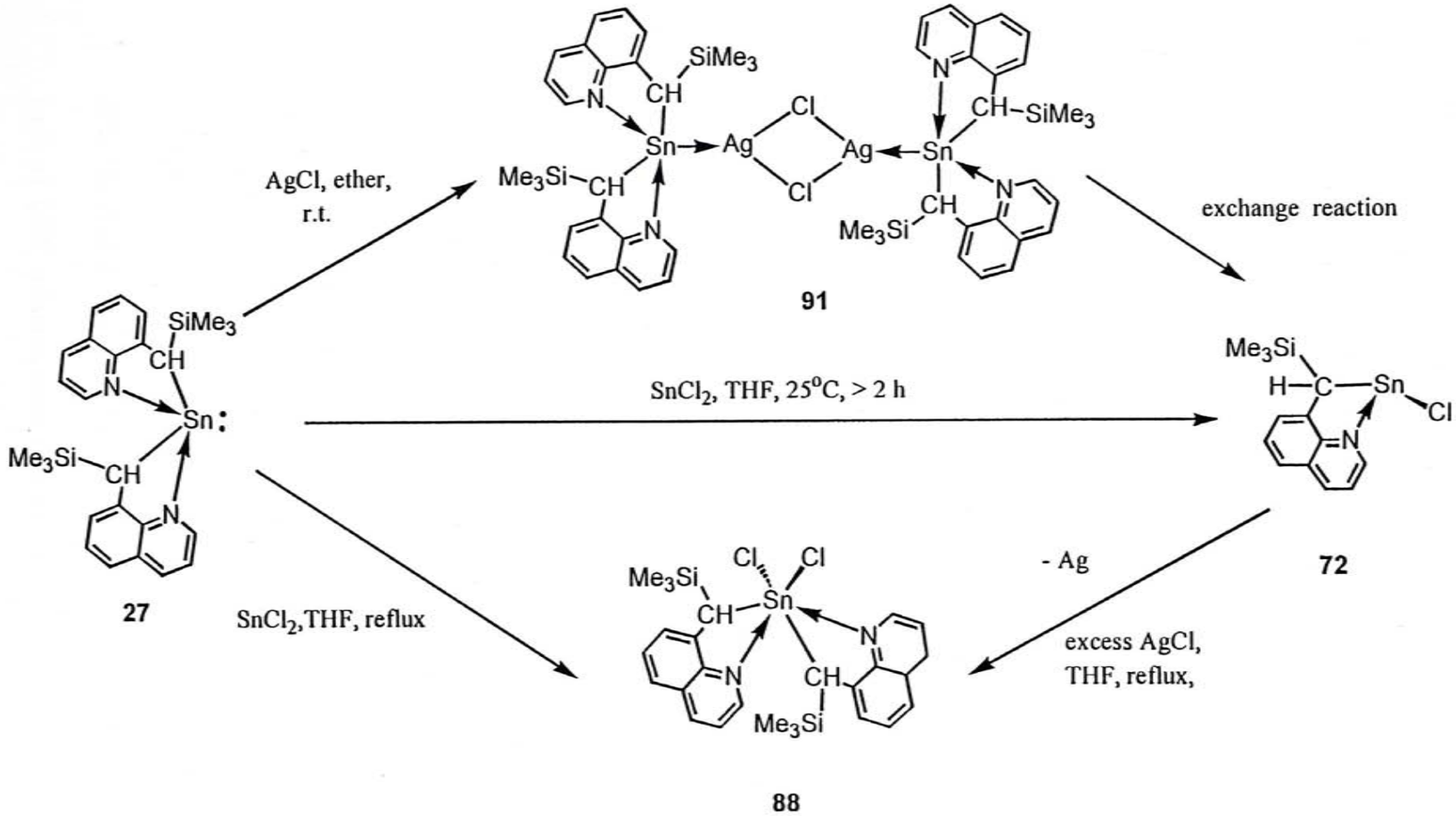


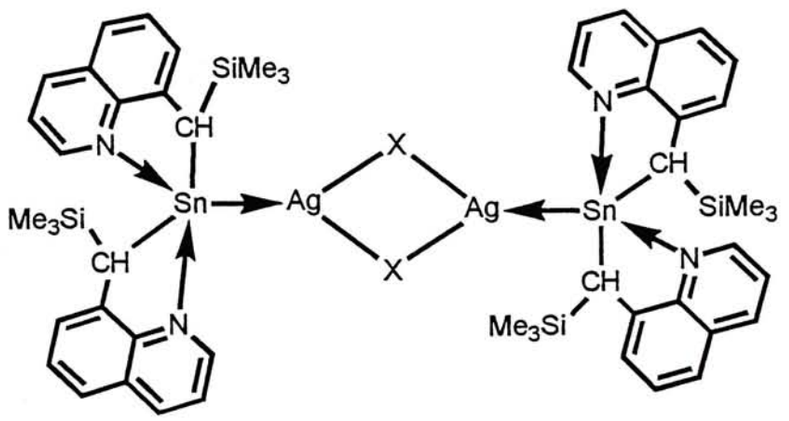
Figure 3.3


AgCl, ether,
r.t.
91
exchange reaction
27
SnCl2, THF, 25°C, > 2 h
72
SnCl2,THF, reflux
- Ag
excess AgCl,
THF, reflux,
88

Scheme 3.5

The structures of compounds **92**, **95** and **96** are proposed to be the same structure as compound **91** as they belong to the same group 11 metal derivatives.

The reaction of $[Sn(R^2)_2]$ (**27**) with AgSCN and AgCN were compared with Lappert's work.[13] The structures of $[Ag(SCN)\{Sn(Bsi)_2\}\text{-}(thf)_2]$ (**80**) and $[(1/n)\text{-}[Ag(CN)\{Sn(Bsi)_2\}_n]$ (**81**) were Sn(II)-Ag(I) centrosymmetric dimer which were different from the proposed structure in this work It is due to the presence of vacant *p*-orbitals in the central tin atom non-functionalized alkyl ligand $[\bar{C}H(SiMe_3)_2]$. While $[\bar{C}H(SiMe_3)C_9H_6N\text{-}8]$ is a *C,N*-chelating ligand to tin, the 2 nitrogens have already occupied the vacant *p*-orbitals and no free vacant *p*-orbital for coordination is available. As a result, the proposed structure of compounds **93** and **94** are expected to have the same structure as compound $[(R^2)_2Sn\rightarrow(\mu\text{-}AgCl)]_2$.



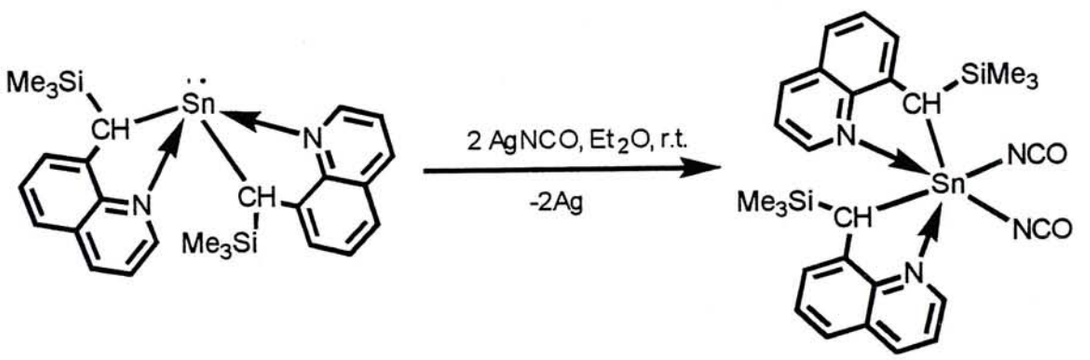
X= SCN (93)
X= CN (94)

Compound **91**, **92**, **93**, **94**, **95** and **96** were found to be light and air-sensitive. Compound $[(R^2)_2Sn\rightarrow CuCl]$ (**95**) was thermally stable at 0 °C and gradually decomposed at higher temperature. All of them showed poor solubility in solvents such as THF, toluene, ether and benzene.

3.2.2 Oxidative-addition (or insertion) reactions of tin(II) compounds

3.2.2.1 Reaction of AgNCO with $[Sn(R^2)_2]$ -Synthesis of $[Sn(R^2)_2(NCO)_2]$ (97)

The oxidative addition reactions of $[Sn(R^2)_2]$ (**27**) with 2 equivalents of AgNCO was carried out at room temperature in ether with the absence of light which gave the oxidative addition adduct of compound $[(R^2)_2Sn(NCO)_2]$ (**97**) and silver metal (**Scheme 3.6**). Compound **97** was obtained as colorless crystals. It is soluble in THF and hydrocarbon solvent such as toluene and benzene. Single crystals of compound **97** suitable for X-ray structural analysis were obtained by recrystallization from toluene. Similar reaction of $[Sn(Bsi)_2]$ with AgNCO to give $[(Bsi)_2Sn(NCO)_2]$ (**85**) has been reported by Lappert and coworkers.[13]



(**27**) (**97**)

Scheme 3.6

3.2.3 Spectroscopic properties of compounds 91-97

The ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopic data of **91** and **97** are consistent with the X-ray crystal structures determination. Compound **97** is soluble in non-polar solvent such as toluene and it is found to be air-stable. While compounds **91-96** show poor solubility in solvents such as THF, toluene, ether and benzene.

Compounds **91-97** have been characterized by mass spectrometry, ^{1}H and ^{13}C spectroscopy. The physical properties for compound **91-97** are shown in Table 3.2

Table 3.2. Some physical properties for compounds 91 – 97

Compounds	*Appearance*	*m.p.,°C*[a]	*Yield, %*
$[(R^2)_2SnAgCl]_2$ (**91**)	Yellow	190-192 (dec.)	58
$[(R^2)_2SnAgI]_2$ (**92**)	Orange	222-225 (dec.)	53
$[(R^2)_2SnAgSCN]_2$ (**93**)	Colorless	174-176 (dec.)	61
$[(R^2)_2SnAgCN]_2$ (**94**)	Colorless	172-177 (dec.)	74
$[(R^2)_2SnCuCl]_2$ (**95**)	yellow	213-215 (dec.)	14
$[(R^2)_2SnCuI]_2$ (**96**)	Orange	214-216 (dec.)	56
$(R^2)_2Sn(NCO)_2$ (**97**)	Colorless	193-196 (dec.)	60

[a] m.p. were measured in capillary tubes sealed under nitrogen and were uncorrected.

The mass spectra of compounds **91**, **93** and **94** showed peaks at 574, 584 and 606 respectively, which were assigned to $[M-Ag]^+$ rather than parent peak. The absence of parent peaks in mass spectra of compounds **91**, **93** and **94** suggest that the ease of ionization of these compounds by losing one silver atom in vapor phase. Similarly, compound **97** shows peak at 590 rather than the parent peak, which is assigned to $[M-NCO]^+$. It is also indicated the ease of ionization of one NCO in

vapor phase. The mass spectra of **92** show peak at 655 which are due to $[M-I]^+$, it suggests that the ease of breaking metal-iodide bond.

The ^1H NMR spectra of **91-97** show similar patterns and having one unique types of signals due to the alkyl ligand R^2. The tin satellites (^{119}Sn, 85%, I = 1/2) of the methine protons of the alkyl ligands R^2 were observed in ^1H NMR spectra of compounds **91-97**. The coupling constant $^2J(^{119}Sn, ^1H)$ lie in the range 3.6 - 87 Hz. The coupling constant $^2J(^{119}Sn, ^1H)$ of 57 Hz in compound **91**, which is larger than the value of 19.8Hz in $(R^2)_2Sn\rightarrow SnCl_2$ coupling. The coupling constants $^2J(^{119}Sn, ^1H)$ of 54 Hz in **97** is significantly smaller than those values in the dialkyltin(IV) dihalides $(R^2)_2SnF_2$ (**87**), $(R^2)_2SnCl_2$ (**88**), $(R^2)_2SnBr_2$ (**89**), $(R^2)_2SnI_2$ (**90**) (95.8 - 116.6 Hz). The chemical shift of **91-97** of methine protons (δ1.28 - 2.75) are significantly down field than the values of 1.16 in the parent tin(II) compound $[(R^2)_2Sn]$ (**27**), indicating the coordination of group 11 derivatives to compound $[(R^2)_2Sn]$ affect the shielding of the methine protons. The $^{13}C\{^1H\}$ NMR spectra of **91-97** are normal and show the expected nine types of aromatic carbons in ligand R^2

Table 3.3. **^{1}H NMR spectral data for compounds 91-97[a]**

Compounds	*Me_3Si*	*CH*	*$^2J(^{119}Sn, ^1H)$, Hz*	*Aromatic*
$[(R^2)_2SnAgCl]_2$ (**91**)	0.31	2.75	57.00	6.42 (dd), 6.53 (dd), 6.64 (m), 6.99 (dd), 8.29 (m)
$[(R^2)_2Sn\ AgI]_2$ (**92**)	0.12	1.39	3.60	6.72 (dd), 6.84 (d), 6.93 (d), 7.02 (d), 7.42 (d), 9.60 (d)
$[(R^2)_2SnAgSCN]_2$ (**93**)	-0.03	1.28	21.00	6.70 (dd), 6.76 (d), 6.93 (dd), 6.98 (d), 7.41 (d), 9.07 (d)
$[(R^2)_2SnAgCN]_2$ (**94**)	-0.06	1.81	87.00	6.72 (d), 6.82 (br), 6.86 (d), 7.41 (s), 7.49 (d), 9.13 (s)
$[(R^2)_2Sn\ CuCl]_2$ (**95**)	0.10	1.40	6.60	6.64 (dd), 6.79(d), 6.98 (m), 7.42 (d), 9.27 (br)
$[(R^2)_2Sn\ CuI]_2$ (**96**)	0.18	1.35	14.10	6.67 (dd), 6.81 (d), 6.97 (m), 7.42 (dd), 9.72 (dd)
$[(R^2)_2Sn(NCO)_2]$ (**97**)	0.18	2.35	54.00	6.40 (dd), 6.51 (dd), 6.62(t), 6.97 (dd), 8.14 (dd)

[a] chemical shifts are in δ (ppm) referenced to internal C_6D_6 (δ 7.15 ppm), 300.13 MHz.

Table 3.4. **$^{13}C\{^{1}H\}$ NMR spectral data for compounds 91-97[a]**

Compounds	*Me_3Si*	*$CSiMe_3$*	*-CN/-NCO*	*Aromatic*
$[(R^2)_2SnAgCl]_2$ (**91**)	-0.49	43.42		121.04, 122.35, 126.22, 129.03, 137.17, 140.53, 142.53, 142.79, 146.84
$[(R^2)_2Sn\ AgI]_2$ (**92**)	-0.23	31.23		121.26, 121.94, 129.09, 130.51, 138.55, 146.17, 148.09, 148.23
$[(R^2)_2SnAgSCN]_2$ (**93**)	-0.61	30.80	1.36	121.45, 122.07, 125.64, 130.55, 131.67, 138.62, 145.53, 147.35, 147.66
$[(R^2)_2SnAgCN]_2$ (**94**)	-0.16	45.18	56.23	121.36, 122.39, 125.66, 129.29, 130.78, 139.14, 145.77, 147.40, 147.87
$[(R^2)_2Sn\ CuCl]_2$ (**95**)	-1.16	22.19		120.82, 121.19, 124.18, 126.39, 130.51, 135.90, 147.77, 148.82
$[(R^2)_2Sn\ CuI]_2$ (**96**)	-0.04	30.98		121.10, 121.84, 125.64, 129.15, 130.38, 138.45, 146.43, 148.16, 148.74
$[(R^2)_2Sn(NCO)_2]$ (97)	-0.02	37.59	2.02	122.11, 123.81, 127.58, 129.79, 138.91, 139.68, 143.38, 147.68

[a] chemical shifts are in δ (ppm) referenced to internal C_6D_6 (δ 128.00 ppm), 75.47 MHz.

Table 3.5. **^{119}Sn NMR of compounds 92, 93, 96, 97**

Compounds	*δ, ppm*[a]	*References*
$[(R^2)_2Sn\ AgI]_2$ (**92**)	5.38	This work
$[(R^2)_2SnAgSCN]_2$ (**93**)	-246.31	This work
$[(R^2)_2Sn\ CuI]_2$ (**96**)	90.27	This work
$[(R^2)_2Sn(NCO)_2]$ (**97**)	19.89	This work
$[Ag(SCN)\{Sn(Bsi)_2\}\text{-}(thf)_2]$ (**80**)	250.00	13
$Ag(PPh_3)_3SnCl_3$ (**75**)	2.61	10
$[\{Sn(Bsi)_2(NCO)_2]$ (**85**)	-47.00	13

[a] recorded in C_6D_6 and referenced to external $SnMe_4$ at 298 K

The ^{119}Sn NMR spectra of **92**, **93**, **96** and **97** showed peaks at δ 5.38, -246.31, 90.27 and 19.89 ppm respectively. They are more upfield shift than the signal of δ 141.73 for the parent compound $[(R^2)_2Sn]$ (**27**). The ^{119}Sn NMR chemical shift of compound **93** and **97** are significantly more upfield than similar compound **80** and **85**, respectively.

Table 3.6. **IR Spectral data of compounds 93, 94, 97**

Compounds	*vcm^{-1}*[a]
$[(R^2)_2SnAgSCN]_2$ (**93**)	2098.04
$[(R^2)_2SnAgCN]_2$ (**94**)	2134.35
$[(R^2)_2Sn(NCO)_2]$ (**97**)	2223.59, 846.83

The peaks at 2098.04 cm^{-1}, 2134.35 cm^{-1} were assigned to the C=N double bond and C≡N triple bond of compounds **93** and **94** respectively. Two peaks were

bond and C≡N triple bond of compounds **93** and **94** respectively. Two peaks were obtained in compound **97**, 2223.59 cm^{-1} and 836.83 cm^{-1}, assigned to C≡N triple bond and C-O single bond in $[(R^2)_2Sn(NCO)_2]$ (**97**). The down field shift of the stretching frequencies of C≡N are due to the $p\pi \rightarrow d\pi$ donation of nitrogen to the metal center and decrease in the bond order of π orbital.

3.2.4 Molecular structure of $[\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Sn\rightarrow(\mu\text{-}AgCl)]_2$ (91)

The molecular structure of **91** with atom numbering schemes is shown in Figure 3.4. Selected bond distances (Å) and bond angles (°) are shown in Table 3.8.

The compound $[\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Sn\rightarrow(\mu\text{-}AgCl)]_2$ (**91**) is a centrosymmetric dimer with C_2 symmetry. It is binuclear, isomorphous to $[\{(C_6H_{11})_3P\}Ag(\mu\text{-}Cl)_2Ag\{P(C_6H_{11})_3\}]$ (**98**) and $[\{(C_6H_{11})_3As\}Ag(\mu\text{-}Cl)_2Ag\{As\text{-}(C_6H_{11})_3\}]$[24] (**99**), the silver environment being quasi-trigonal planar.

The alkyl ligand $\bar{R}^2$ is bonded in a *C,N*-chelate fashion to the Sn(1) atom, which adopts a penta-coordinated square-pyramidal geometry. The Sn(1) atom is bonded directly to Ag(1) of the AgCl fragment with a Sn-Ag distance of 2.58(7) Å, which is similar to the distance of 2.60(1) Å in $[Ag(SCN)\{Sn(Bsi)_2\}\text{-}(thf)_2]$ (**80**). The plane containing C(10), Sn(1), C(23) is nearly perpendicular (98.9°) to the plane of Cl(1)#1-Ag(1)-Cl(1) (92.5°), which is consistent with the bonding model as described in Figure 3.3. The Sn-C distance of 2.20 Å (av.) and Sn-N distance of 2.40 Å (av.) are significantly shorter than the corresponding distances of 2.26 Å and 2.51 Å (av.) in the parent compound $[Sn(R^2)_2]$ (**27**). This is presumably a consequence of reduced electron density at AgCl. The covalent Ag-Cl distance of 2.86(13) Å is relatively longer than the AgCl distance of 2.77 Å in the argentous chloride. However, dative Ag-Cl of 2.44 (13) Å is comparable to the covalent Ag-Cl distance of 2.64(2) Å and dative Ag-Cl distance of 2.46(1) Å in the Ag-Cl complex $[\{(C_6H_{11})_3As\}Ag(\mu\text{-}Cl)_2Ag\{As(C_6H_{11})_3\}]$ (**99**)

The angle sum of Cl(1)#1-Ag(1)-Cl(1) and Ag(1)#1-Cl(1)-Ag(1) is 180° which is comparable to the angle sum of Ag-Cl-Ag' and Cl-Ag-Cl' in $[\{(C_6H_{11})_3As\}Ag(\mu\text{-}Cl)_2Ag\{As(C_6H_{11})_3\}]$ (**99**) (180°).

Table 3.7. Comparison of some structural data of compound 91

Compounds	*Ag-Cl(Å)*	*Sn-Ag(Å)*	*Cl-Ag-Cl(°)*	*Ag-Cl-Ag(°)*	*References*
$[(R^2)_2Sn\rightarrow(\mu\text{-}AgCl)]_2$	2.86(13)	2.58(7)	92.51(4)	87.49(4)	This work
(**91**)	2.44(13), (dative)				
$[\{(C_6H_{11})_3As\}AgCl]_2$	2.64(2)		97.03(5)	82.97(4)	24
(**99**)	2.46(1), (dative)				
$[Ag(SCN)\{Sn(Bsi)_2\}$		2.60(1)			13
$-(thf)_2]$ (**80**)					

Table 3.8. Selected bond distances (Å) and angles (°) for compound 91

$[\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Sn\rightarrow(\mu\text{-}AgCl)]_2$ (**91**)

Sn(1)-Ag(1)	2.58(7)	Sn(1)-N(1)	2.423(4)
Sn(1)-N(2)	2.379(3)	Ag(1)-Cl(1)#1	2.439(13)
Ag(1)-Cl(1)	2.859(13)	Sn(1)-C(23)	2.225(5)
Sn(1)-C(10)	2.183(4)	C(8)-C(10)	1.462(6)
Si(1)-C(10)	1.908(5)		
Cl(1)#1-Ag(1)-Sn(1)	154.37(3)	Cl(1)#1-Ag(1)-Cl(1)	92.51(4)
Sn(1)-Ag(1)-Cl(1)	111.96(3)	Ag(1)#1-Cl(1)-Ag(1)	87.49(4)
N(2)-Sn(1)-Ag(1)	98.91(8)	N(2)-Sn(1)-N(1)	156.57(11)
C(10)-Sn(1)-N(2)	90.18(14)	C(10)-Sn(1)-N(1)	74.2(2)
C(10)-Sn(1)-C(23)	98.9(2)	C(23)-Sn(1)-Ag(1)	134.24(10)
C(23)-Sn(1)-N(2)	75.67(14)		

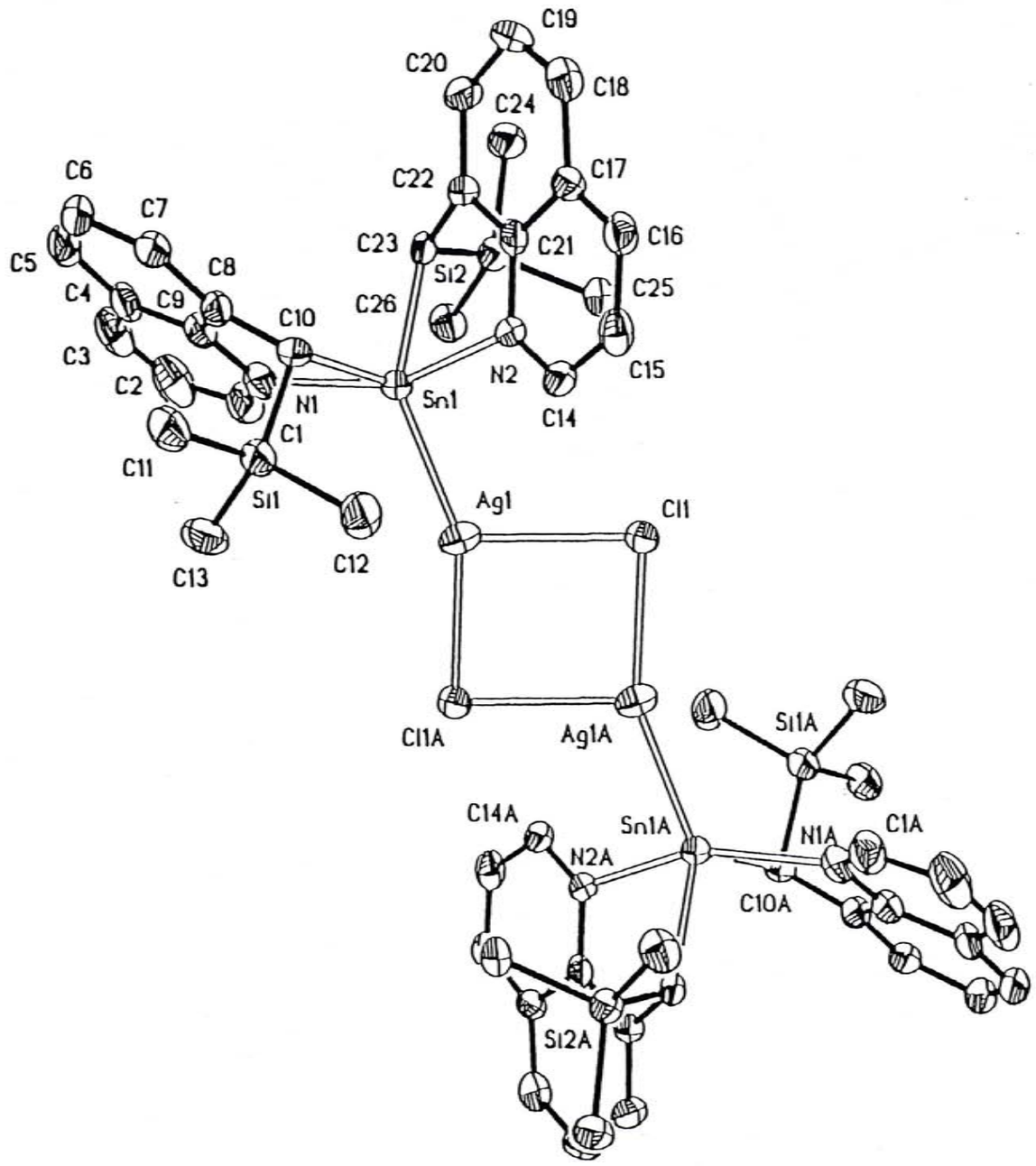


Figure 3. 4 Molecular Structure of $[\{CH(SiMe_3)C_9H_6N\text{-}8)\}_2Sn\rightarrow(\mu\text{-}AgCl)]_2$ (91)

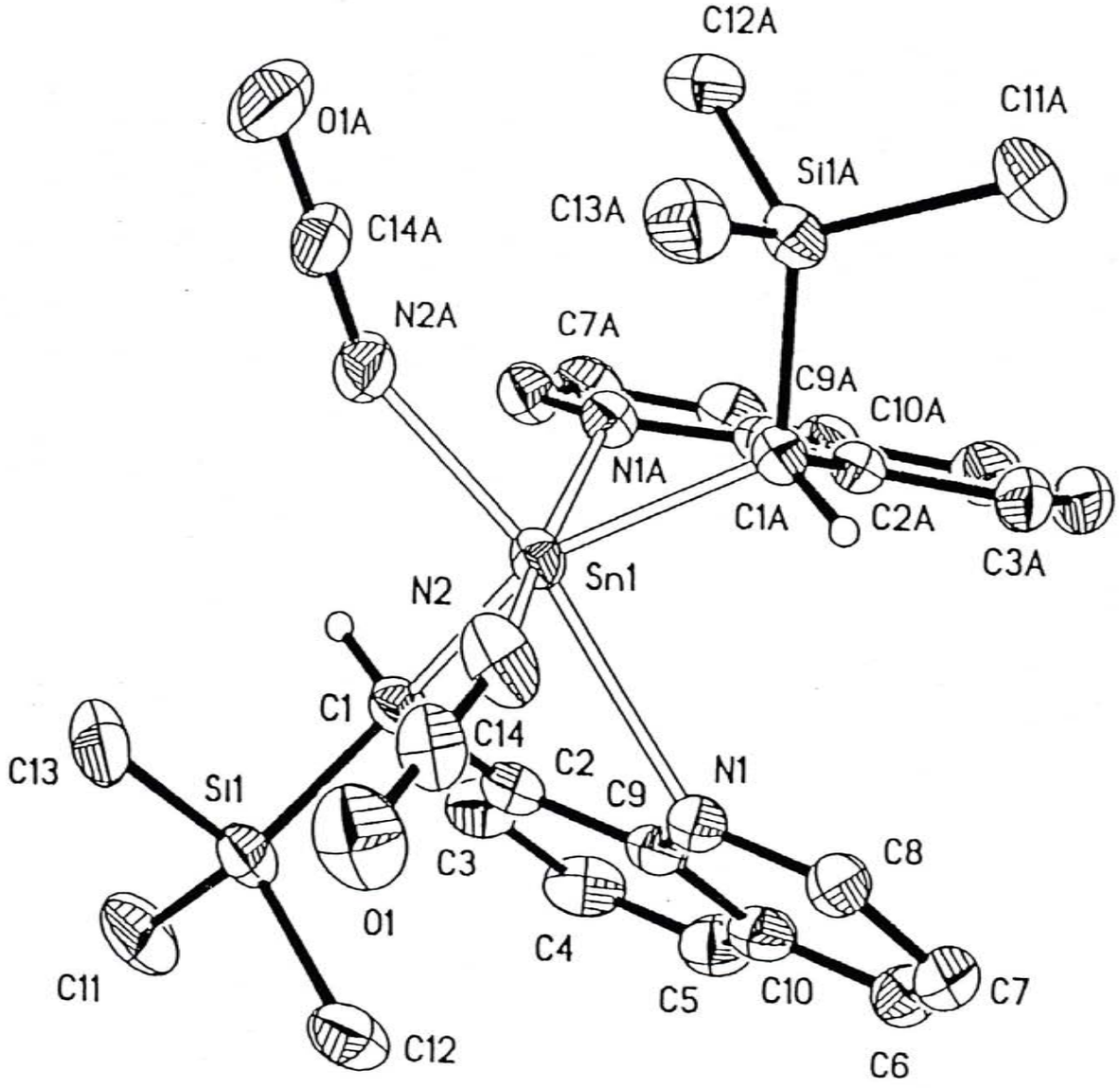


Figure 3. 5 Molecular Structure of [{CH(SiMe$_3$)C$_9$H$_6$N-8)}$_2$Sn(NCO)$_2$] (97)

3.2.5 Molecular structure of [{CH(SiMe$_3$)C$_9$H$_6$N-8}$_2$Sn(NCO)$_2$] (97)

The molecular structure of **97** with atom numbering schemes is shown in Figure 3.5. Selected bond distances (Å) and bond angles (°) is shown in Table 3.9. Compound **97** is an oxidative addition adduct and can be compared with compound [(Bsi)$_2$Sn(NCO)$_2$] (**85**).[13]

The dialkyl tin(IV) compound **97** crystallizes in a monoclinic P2/c (No.2) space group. The two alkyl ligand, $\bar{R}^2$ are bonded to the central tin atom in *trans C,N*-chelating fashion. The two NCO groups are bonded to the central tin atom in *cis* position, which are both *trans* to nitrogen donors' atoms of alkyl ligands $\bar{R}^2$. In this compound, the four atoms N(2)#1, N(2), N(1)#1, N(1), make a least-square plane and the tin atom is nearly coplanar to this plane. The Sn(1)-N(2) and O(1)-C(14) of 2.12(2) Å and 1.18(4), are longer than that of 2.06(7) Å and 1.19 Å (av.) in compound **85**, respectively. This is presumably due to the size of [$\bar{C}$H(SiMe$_3$)C$_9$H$_6$N-8] is more bulky than that of [$\bar{C}$H(SiMe$_3$)$_2$] in compound **85**.

It has been shown that the tin atom is nearly coplanar to the plane of N(2)#1, N(2), N(1)#1, N(1). Therefore, the coordination geometry at tin can be described as distorted octahedral with N(2)#1, N(2), N(1)#1, N(1) as the square plane, C(1)#1 and C(1) in mutual *trans* positions occupying the apices of the distorted octahedral. The C(1)-Sn(1)-C(1)#1, N(2)#1-Sn(1)-N(1) and N(2)-Sn(1)-N(1)#1 bond angles of 143.08(3)°, 169.69(7)° and 169.69(7)°, are deviated significantly from ideal octahedral bond angles value of 180°, probably due to the bulky ligand [$\bar{C}$H(SiMe$_3$)C$_9$H$_6$N-8]. The N(2)-Sn(1)-N(2)#1 angle of 90.9(2)° is comparable to the angle of 94.6(3)° in compound **85**, which is significantly different because of different in coordination geometry.

Table 3.9. Selected bond distances (Å) and angles (°) for compound 97

$[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}_2(NCO)_2]$ (97)			
Sn(1)-N(2)	2.116(2)	Sn(1)-N(2)#1	2.116(2)
Sn(1)-C(1)	2.145(2)	Sn(1)-C(1)#1	2.145(2)
O(1)-C(14)	1.181(4)	N(2)-C(4)	1.127(4)
Sn(1)-N(1)	2.487(2)	Sn(1)-N(1)#1	2.497(2)
N(2)-Sn(1)-N(2)#1	90.9(2)	N(2)-Sn(1)-C(1)	107.87(9)
N(2)#1-Sn(1)-C(1)	97.89(9)	N(2)-Sn(1)-C(1)#1	97.89(9)
N(2)#1-Sn(1)-C(1)#1	107.87(9)	C(1)-Sn(1)-C(1)#1	143.08(3)
N(2)-Sn(1)-N(1)#1	169.69(7)	N(2)#1-Sn(1)-N(1)#1	87.42(9)
C(1)#1-Sn(1)-N(1)#1	82.44(7)	C(1)#1-Sn(1)N(1)#1	73.00(8)
N(2)-Sn(1)-N(1)	87.42(9)	N(2)#1-Sn(1)-N(1)	169.69(7)
C(1)-Sn(1)-N(1)	73.00(8)	C(1)#1-Sn(1)-N(1)	82.44(7)
N(1)#1-Sn(1)-N(1)	95.98(9)	C(14)-N(2)-Sn(1)	154.8(2)
N(2)-C(14)-O(1)	178.03(3)		

APPENDIX I

A. Experimental Procedures for Chapter 1

Materials:

$GeCl_2$.dioxane was prepared according to literature procedure.[9] Anhydrous $SnCl_2$ (Fluka), 2-picoline (Aldrich), Benzonitrile (Aldrich), 8-methylquinoline (Aldrich) were used as purchased without further purification. 8-(trimethylsilyl)-methyl-quinoline,[38] $[LiR^2(tmeda)]$[38] 2-[Bis(trimethylsilyl)methyl]pyridine[34] and $[Li(R^1)]$ (**28**)[32] were prepared according to literature procedure.

Synthesis of $[Ge\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}\{C(C_5H_4N\text{-}2)C(Ph)N\text{-}(SiMe_3)_2]$ (29) ***$[Ge(R^1R^{1'})]$***

To a solution of $(LiR^1)_2$ (**28**) (3.75 g, 5.41 mmol) in diethyl ether (30 mL) was added slowly to a suspension of $GeCl_2$·dioxane (1.25 g, 5.41 mmol) in ether (25 mL) at 0 °C, and was then raised to room temperature. The orange mixture was stirred for further 16 h at room temperature. The solvent was then removed in *vacuo* and the residue was extracted with toluene (50 mL). Insoluble solid in the extract was separated by filtration and the orange residue was concentrated and n-hexane (5 mL) was added and the solution was kept at 4 °C for 1 day to yield 2.55 g (62%) orange crystals of *title compound* **29**. m.p. 206-208 °C (dec.). Anal. Found: C, 60.69; H, 7.19; N, 7.70%. Calcd. for $C_{38}H_{54}Si_4N_4Ge$: C, 60.75; H, 7.19; 7.46%. EI-MS: *m/z* 752 $[M]^+$, 412 $[M\text{-}R^1]^+$. ^1H NMR (C_6D_6, 300.13 MHz): δ -0.04 (s, $SiMe_3$, 9 H), 0.06 (s, $SiMe_3$, 18H), 0.21 (s, $SiMe_3$, 9H), 6.52 (t, J = 6.3 Hz, py, 1H), 6.67 (br, py, 1H), 7.05 (m, Ph, 5H), 7.12 (br, py, 3H), 7.50 (m, Ph, 5H), 7.77 (d, J = 6.9 Hz, py, 2H), 8.59 (d, J = 4.8 Hz, py, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ 2.94, 3.02, 3.11

($SiMe_3$), 114.21 ($CSiMe_3$), 117.93, 118.98, 119.13, 123.73, 124.20, 124.96, 125.59, 127.39, 127.79, 128.33, 128.79, 129.00, 130.69, 131.13, 135.05, 136.66, 144.09, 145.31, 147.22, 147.99, 150.80, 153.57 (aryl C), 155.88 (py*C*Ge), 166.79, 171.46 (N*C*Ph).

Synthesis of [Sn{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$] (30) ***[Sn(R^1)$_2$]***

To a solution of (LiR^1)$_2$ (**28**) (0.71 g, 1.02 mmol) in diethyl ether (30 mL) was added slowly to a suspension of $SnCl_2$ (0.19 g, 1.02 mmol) in ether (25 mL) at 0 °C, and was then raised to room temperature. The yellow mixture was stirred for 16 h at ambient temperature. The solvent was then removed in *vacuo* and the residue was extracted with toluene (50 mL). Insoluble solid in the extract was removed by filtration and the yellow residue was concentrated and *n*-hexane (5 mL) was added and kept at 4 °C for 1 day to yield 0.42 g (52%) yellow crystals of *title compound* **30**. m.p. 149-151 °C (dec.). Anal. Found: C, 56.82; H, 6.83; N, 6.94%. Calcd. for $C_{38}H_{54}Si_4N_4Sn$: C, 57.20; H, 6.82; N, 7.02%. EI-MS: *m/z* 798 $[M]^+$, 459 $[M\text{-}R^1]^+$, 339 $[R^1]^+$. ^{1}H NMR (C_6D_6, 300.13 MHz): δ -0.16 (s, $SiMe_3$, 9H), -0.03 (s, $SiMe_3$, 9H), -0.01 (s, $SiMe_3$, 9H), 0.22 (s, $SiMe_3$, 9H), 6.49 (br, py, 2H), 6.57 (m, py, 4H), 7.08 (m, Ph, 5H), 7.49 (m, py, 6H), 7.75 (d, J = 6.90 Hz, Ph, 5H), 8.83 (br, py, 2H), 9.09 (br, py, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ 1.38, 2.41, 3.65, 4.59 ($SiMe_3$), 118.08, 118.77 ($CSiMe_3$), 118.87, 123.91, 124.10, 124.80, 125.64, 127.23, 127.68, 128.56, 129.28, 130.47, 131.12, 135.20, 135.58, 137.07, 141.95, 144.29, 146.06, 147.51, 147.68, 147.98, 151.68, 158.76, 159.24 (aryl C), 168.17, 173.09 (N*C*Ph). ^{119}Sn NMR (C_6D_6, 149.2 MHz, $SnMe_4$ (ext.)): δ -140 (s).

Synthesis of $[Sn\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}_2Cl_2]$ (31) ***$[Sn(R^1)_2Cl_2]$***

To a solution of $(LiR^1)_2$ (**28**) (3.00 g, 4.34 mmol) in diethyl ether (30 mL) was added slowly to a suspension of $SnCl_4$ (1 M, 4.34 mL, 4.34 mmol) in ether (25 mL) at 0 °C, and was then raised to room temperature. The yellow mixture was stirred for 16 h at ambient temperature. The solvent was then removed in vacuo and the residue was extracted with toluene (50 mL). Insoluble solids were removed by filtration and the yellow residue was concentrated and n-hexane (5 mL) was added and kept at 4 °C for 1 day to yield 2.18 g (58%) yellow crystals of *title compound* **31**. m.p. 227-230 °C (dec.). Anal. Found: C, 52.51; H, 6.03; N, 6.58%. Calcd. for $C_{38}H_{54}N_4Si_4SnCl_2$: C, 52.53; H, 6.26; N, 6.45%. FAB-MS: *m/z* 833 $[M\text{-}Cl]^+$, 798 $[M\text{-}Cl\text{-}Cl]^+$. ^1H NMR (C_7D_8, 300.13 MHz): δ -0.02, 0.03 (s, $SiMe_3$, 36H), 6.09 (td, J = .2 Hz, 1.2 Hz, py, 2H), 6.90 (m, py, 2H), 6.98-7.20 (m, 8H, Ph), 7.60 (s, Ph, 2H), 7.99 (t, J = 6.0 Hz, py, 2H), 8.5 (d, J = 3.0 Hz, py, 2H). $^{13}C\{^1H\}$ NMR (C_7D_8, 75.47 MHz): δ -2.78, 0.96 ($SiMe_3$), 107.69 ($CSiMe_3$), 112.89, 119.68, 121.56, 124.583, 126.06, 130.69, 132.36, 132.66, 139.22, 140.21, 160.27 (aryl C), 164.34 (NCPh). ^{119}Sn NMR (C_6D_6, 149.2 MHz, $SnMe_4$ (ext.)): δ 82.54 (s).

B. Experimental Procedures for Chapter 2

Materials:

Sulfur and selenium powder were purchased from Aldrich Chemical Co. and used without furter purification.

Synthesis of [{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)$_2$}-Ge=S] (59) [(R^1)(R$^{1'}$)Ge=S]

To a solution of [Ge(R^1)(R$^{1'}$)] (**29**) (0.73 g, 0.97 mmol) in toluene (30 mL) was added slowly to a suspension of sulfur (0.03 g, 0.97 mmol) in toluene (25 mL) at 0 °C. The yellow mixture was warmed to room temperature and stirred for 16 h at room temperature. The solvent was concentrated and cooled to afford the yellow solid. After washing the yellow solid with cold pentane and dried in vacuo, yielded 0.23 g (42%). m.p. 222-226 °C (dec.). Anal. Found: C, 58.07; H, 7.05; N, 7.74%. Calcd. for. $C_{38}H_{54}N_4Si_4GeS$: C, 58.22; H, 6.94; N, 7.14%. EI-MS: *m/z* 784 [M]$^+$, 752 [M-S]$^+$, 680 [M-S-R^1]$^+$. ^{1}H NMR (C_6D_6, 300.13 MHz): δ 0.03 (s, SiMe$_3$, 9H), 0.14 (s, SiMe$_3$, 27H), 6.24 (t, J = 6.0 Hz, py, 2H), 6.84 (br, py, 2H), 6.81 (m, Ph, 2H), 6.92 (td, J = 8.7 Hz, 1.5 Hz, py, 2H), 7.04 (d, J = 7.2 Hz, Ph, 1H), 7.12 (t, J = 7.5 Hz, Ph, 2H), 7.19 (m, Ph, 2H), 7.44 (m, py, 1H), 7.81 (d, J = 7.5 Hz, py, 2H), 8.85 (dd, J = 5.7 Hz, 4.2 Hz, py, 2H). ^{13}C{^{1}H} NMR (C_6D_6, 75.47 MHz): δ 2.66, 3.06, 3.94 (SiMe$_3$), 111.68 (*C*SiMe$_3$), 117.56, 119.81, 120.06, 120.41, 120.74, 123.95, 124.64, 126.04, 126.82, 129.84, 130.06, 130.38, 130.85, 132.01, 135.21, 135.60, 138.72, 139.20, 143.33, 144.14, 144.65, 148.61, 156.56 (aryl C), 157.65 (py*C*Ge), 161.31, 169.39 (N*C*Ph).

Synthesis of [{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)$_2$}-Ge=Se] (60) ***[(R^1)(R$^{1'}$)Ge=Se]***

To a stirring suspension of selenium powder (0.73 g, 0.97 mmol) in toluene (15 mL) was added dropwise with a solution of [Ge(R^1)(R$^{1'}$)] (**29**) (0.08 g, 0.97 mmol) in toluene (15 mL) at 0 °C. The resultant yellowish orange solution was allowed to warm to room temperate and stirred for 18 h. Excess selenium powder was separated by filtration. The filtrate was concentrated and stored at -30 °C, yielded 0.50 g (62%) yellowish orange crystal of *title compound* **60**. m.p. 233-236 °C (dec.). Anal. Found: C, 55.00; H, 6.67; N, 7.39%. Calcd. for $C_{38}H_{54}N_4Si_4GeSe$: C, 54.94; H, 6.55; N, 6.75%. FAB-MS: *m/z* 830 [M-Se]$^+$. ^{1}H NMR (C_6D_6, 300.13 MHz): δ 0.10, 0.21 (s, SiMe$_3$, 36H), 6.27 (br, py, 2H), 6.94 (t, *J* = 7.8 Hz, py, 2H), 7.06 (d, *J* = 9.9 Hz, py, 2H), 7.19-7.24 (m, Ph, 10H), 7.43 (br, py, 1H), 7.92 (br, py, 1H), 9.05 (d, *J* = 2.7 Hz, py, 1H). ^{13}C{^{1}H} NMR (C_6D_6, 75.47 MHz): δ 2.72, 3.13, 4.36 (SiMe$_3$), 112.44 (*C*SiMe$_3$), 119.83, 120.77, 123.87, 124.17, 126.90, 126.99, 127.36, 129.28, 129.86, 130.27, 132.14, 135.25, 136.70, 138.97, 139.23, 144.25, 144.56, 145.07, 148.28, 156.30, 157.28, 159.89 (aryl C), 161.71 (py*C*Ge), 168.03, 169.27 (N*C*Ph)

Synthesis of [N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$Sn=S] (61) ***[(R^1)$_2$Sn=S]***

To a stirring solution of powdered sulfur (0.04 g, 1.14 mmol) in toluene (20 mL) was added dropwise a solution of [Sn(R^1)$_2$] (**30**) (0.91 g, 1.14 mmol) in toluene at 0 °C. The resultant orange solution was allowed to warm to room temperate and stirred for 18 h. The solution was concentrated and kept at -30 °C, afforded yellow crystal of *title compound* **61**, 0.65 g (69%). m.p. 246-248°C (dec.). Anal. Found: C, 57.57; H, 6.67; N, 6.60%. Calcd. for $C_{38}H_{54}N_4Si_4SnS.1/2C_7H_8$: C, 56.98; H, 6.63; N, 6.41%. FAB-MS: *m/z* 798 [M-S]$^+$. ^{1}H NMR (C_6D_6, 300.13 MHz): δ 0.04 (s,

$SiMe_3$, 36H), 6.58 (td, J = 7.2 Hz, 1.2 Hz, py, 2H), 6.95-7.13 (m, Ph, 10H), 7.35 (d, J = 8.1 Hz, py, 2H), 7.58 (br, py, 2H), 7.73 (br, py, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ 4.93 ($SiMe_3$), 113.83 ($CSiMe_3$), 119.00, 124.67, 125.65, 129.29, 130.07, 132.69, 134.46, 137.75, 145.13, 149.11, 159.86 (aryl C), 169.46 (NCPh). ^{119}Sn NMR (THF/C_6D_6, 149.2 Hz, $SnMe_4$ (ext.)): δ188.65(s).

Synthesis of [{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}{N(SiMe$_3$)$_2$C(C$_5$H$_4$N-2)C(Ph)Sn=Se}] (62) ***[(R^1)(R$^{1'}$)Sn=Se]***

To a stirring suspension of selenium powder (0.09 g, 1.14 mmol) in toluene (15 mL) was added dropwise with a solution of $[SnR^1]_2$ (**30**) (0.91 g, 1.14 mmol) in toluene (15 mL) at 0 °C. The resultant yellowish orange solution was allowed to warm to room temperate and stirred for 18 h. Excess selenium powder was filtered off, the filtrate was concentrated and stored at -30 °C. Yellowish orange crystal of compound **62** was obtained 0.88 g (89%). m.p. 274-277 °C (dec.). Anal. Found: C, 51.94; H, 6.32; N, 6.28%. Calcd. for $C_{38}H_{54}Si_4N_4SnSe$: C, 52.05; H, 6.21; N, 6.39%. EI-MS: *m/z* 877 $[M]^+$, 798 $[M\text{-}R^1]^+$. ^1H NMR (C_6D_6, 300.13 MHz): δ -0.02 (s, $SiMe_3$, 9H), 0.04 (s, $SiMe_3$, 9H), 0.13 (s, $SiMe_3$, 9H), 0.22 (s, $SiMe_3$, 9H), 6.30 (t, J = 8.7 Hz, py, 1H), 6.61 (m, Ph, 3H), 6.89 (d, J = 6.9 Hz, Ph, 3H), 6.93 (d, J = 8.1 Hz, Ph, 2H), 6.99 (d, J = 5.4 Hz, py, 2H), 7.11 (d, J = 3.9 Hz, py, 2H), 7.22 (d, J = 6.3 Hz, Ph, 2H), 7.64 (d, J = 2.6 Hz, py, 1H), 8.47 (d, J = 6.0 Hz, py, 1H), 9.23 (d, J = 4.5 Hz, py, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ 2.15, 3.15, 3.85 ($SiMe_3$), 119.69 ($CSiMe_3$), 120.51, 124.30, 124.37, 129.33, 130.40, 131.13, 131.44, 136.87, 138.39, 142.55, 145.32, 146.742, 147.69, 147.91, 158.83 (aryl C), 159.49 (NCSn), 161.97, 170.49 (NCPh). ^{119}Sn NMR (THF/C_6D_6, 149.2 Hz, $SnMe_4$ (ext.)): δ-285.92(s).

C. Experimental Procedures for Chapter 3

Materials:

AgNCO, AgSCN, AgCN, anhydrous AgI, CuCl and CuI were purchased from Aldrich Chemical Co. and used without further purification except AgSCN and AgCN were washed by acetone and dried in *vaccuo*. AgCl was prepared by the reaction of $AgNO_3$ and NaCl and washed by acetone and dried in *vaccuo*. $[Sn(R^2)_2]$ **(27)** was prepared according to literature procedure.[25]

Synthesis of $[\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Sn(NCO)_2]$ (97) $[(R^2)_2Sn(NCO)_2]$

To a stirring solution of AgNCO (0.59 g, 3.96 mmol) in diethyl ether (20 mL) was added dropwise with a solution of $[Sn(R^2)_2]$ (**27**) (1.07 g, 1.96 mmol) in ether (25 mL) in the absence of light at ambient temperature. The resultant white solution was stirred for 16 h. After removal of the black solid of silver metal by filtration, the yellow filtrate was concentrated and stored at -30 °C. Colorless crystal of **97** was obtained 0.74 g (60%). m.p. 193-196 °C (dec.). Anal. Found: C, 52.68; H, 5.00; N, 8.72%. Calcd. for $C_{28}H_{32}Si_2SnN_4O_2$: C, 53.26; H, 5.11; N, 8.87%. EI-MS: m/z 590 $[M\text{-}NCO]^+$. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 0.18 (s, $SiMe_3$, 18H), 2.35 (s, $^2J(^{119}Sn, ^1H)$ = 54 Hz, CHSi, 2H), 6.40 (dd, J = 8.1 Hz, 3.6 Hz, aryl H, 2H), 6.51 (dd, J = 7.5 Hz, 5.4 Hz, aryl H, 2H), 6.62 (t, J = 7.2 Hz, aryl H, 4H), 6.97 (dd, J = 8.4 Hz, 6.9 Hz, aryl H, 2H), 8.14 (dd, J = 4.5 Hz, 3.0 Hz, aryl H, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ -0.22 ($SiMe_3$), 2.02 (*N*CO), 37.59 (*C*$SiMe_3$), 122.12, 123.82, 127.58, 128.00, 129.80, 138.92, 139.69, 143.38, 147.68 (C_9H_6N). ^{119}Sn NMR (C_6D_6, 149.2 MHz, $SnMe_4$ (ext.)): δ 19.89 (s).

Synthesis of [{CH(SiMe$_3$)C$_9$H$_6$N-8}$_2$Sn→AgSCN]$_2$ (93) [(R^2)$_2$Sn→AgSCN]$_2$

To a stirring suspension of solid AgSCN (0.14 g, 0.86 mmol) in diethyl ether (20 mL) was added dropwise with a solution of [Sn(R^2)$_2$] (**27**) (0.47 g, 0.86 mmol) in ether (25 mL) in the absence of light at ambient temperature. The resultant white suspension was stirred for 16 h. After isolating the white solid by filtration, the resultant yellow filtrate was concentrated and stored at -30 °C. Colorless crystals of **93** were obtained yield 0.37 g (61%). m.p. 174-176 °C (dec.). Anal. Found: C, 44.78; H, 4.56; N, 4.94%. Calcd. for $C_{27}H_{32}N_3Si_2SnS$: C, 45.46; H, 4.52; N, 5.89%. EI-MS: m/z 695 $[M-N]^+$, 606 $[M-Ag]^+$, 569 $[M-Ag-S]^+$. ^{1}H NMR C_6D_6, 300.13 MHz): δ -0.03 (s, $SiMe_3$, 18H), 1.28 (s, $^2J(^{119}Sn, ^1H)$ = 21 Hz, CHSi, 2H), 6.70 (dd, J = 9.0 Hz, 3.0 Hz, aryl H, 2H), 6.76 (d, J = 4.0 Hz, aryl H, 2H), 6.93 (dd, J = 6.0 Hz, 3.0 Hz, aryl H, 2H), 6.98 (d, J = 9.0 Hz, 2H), 7.41 (d, J = 6.0 Hz, 2H), 9.07 (d, J = 3.0 Hz, aryl H, 2H). ^{13}C{^{1}H} NMR (C_6D_6, 75.47 MHz): δ -0.61 ($SiMe_3$), 1.36 (S*C*N), 30.80 (*C*$SiMe_3$), 121.45, 122.07, 125.64, 130.55, 131.67, 138.62, 145.53, 147.35, 147.66 (C_9H_6N). ^{119}Sn NMR (C_6D_6, 149.2 MHz, $SnMe_4$ (ext.)): δ -246.31 (s).

Synthesis of [{CH(SiMe$_3$)C$_9$H$_6$N-8}$_2$Sn→AgCN]$_2$ (94) [(R^2)$_2$Sn→AgCN]$_2$

To a stirring suspension of solid AgCN (0.21 g, 1.59 mmol) in diethyl ether (20 mL) was added dropwise a solution of [Sn(R^2)$_2$] (**27**) (0.87 g, 1.59 mmol) in ether (25 mL) in the absence of light at room temperature. The resultant white solution was stirred for 16 h. White solid was formed and filtered off, the yellow filtrate was concentrated and stored at -30 °C. Colorless crystals of **94** yielded 0.80 g (74%). m.p. 172-177 °C (dec.). EI-MS: m/z 574 $[M-Ag]^+$, 563 $[M-Ag-C]^+$, 558 $[M-Ag-N]^+$. ^{1}H NMR C_6D_6, 300.13 MHz): δ -0.06 (s, $SiMe_3$, 18H), 1.81 (s, $^2J(^{119}Sn, ^1H)$ = 3.6 Hz, CHSi, 2H), 6.82 (br, aryl H, 2H), 6.86 (d, J = 21 Hz, aryl H, 2H), 7.41 (s, aryl H, 2H),

7.49 (d, J = 9 Hz, aryl H, 2H), 9.13 (s, aryl H, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ -0.17 ($SiMe_3$), 45.17 ($CSiMe_3$), 56.23 (CN), 121.36, 122.397, 125.66, 129.29, 130.78, 139.14, 145.77, 147.40, 147.87 (C_9H_6N)

Synthesis of $[\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Sn\rightarrow(\mu\text{-}AgCl)]_2$ (91) $[(R^2)_2Sn\rightarrow AgCl]_2$

To a stirring suspension of solid AgCl (0.19 g, 1.31 mmol) in diethyl ether (20 mL) was added dropwise a solution of $[Sn(R^2)_2]$ (**27**) (0.72 g, 1.31 mmol) in ether (25 mL) in the absence of light at ambient temperature. The resultant white solution was stirred for 16 h. White solid was formed and filtered off, the yellow filtrate was concentrated and stored at -30 °C. Yellow crystals of **91** yielded 0.52 g (58%). m.p. 190-192 °C (dec.). EI-MS: *m/z* 583 $[M\text{-}Ag]^+$. ^1H NMR C_6D_6, 300.13 MHz: δ 0.31 (s, $SiMe_3$, 18H), 2.75 (s, $^2J(^{119}Sn, ^1H)$ = 57 Hz, CHSi, 2H), 6.42 (dd, J = 8.4 Hz, 3.9 Hz, aryl H, 2H), 6.53 (dd, J = 7.8 Hz, 6.0 Hz, aryl H, 2H), 6.64 (m, aryl H, 4H), 6.99 (dd, J = 8.1 Hz, 6.9 Hz, 2H), 8.29 (m, aryl H, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ -0.49 ($SiMe_3$), 43.42 ($CSiMe_3$), 121.04, 122.35, 126.22, 129.03, 137.17, 140.53, 142.79, 146.84 (C_9H_6N).

Synthesis of $[\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Sn\rightarrow(\mu\text{-}AgI)]_2$ (92) $[(R^2)_2Sn\rightarrow AgI]_2$

To a stirring suspension of solid AgI (0.21 g, 0.90 mmol) in diethyl ether (20 mL) was added dropwise a solution of $[Sn(R^2)_2]$ (**27**) (0.49 g, 0.90 mmol) in ether (25 mL) in the absence of light at 0 °C and raised to ambient temperature. The resultant orange solution was stirred for 16 h. Yellow solid was formed and filtered off, the orange filtrate was concentrated and stored at -30 °C. Orange crystals of **92** yielded 0.37g (53%). m.p. 222-225 °C (dec.). Anal. Found: C, 39.32; H, 4.16; N, 3.84%. Calcd. for $C_{26}H_{32}N_2Si_2SnAgI$: C, 39.92; H, 4.12; N, 3.58%. FAB-MS: *m/z* 655 $[M\text{-}I]^+$. ^1H NMR C_6D_6, 300.13 MHz): δ 0.12 (s, $SiMe_3$, 18H), 1.39 (s, $^2J(^{119}Sn, ^1H)$ = 3.6

Hz, CHSi, 2H), 6.72 (dd, J = 8.1 Hz, 3.9 Hz, aryl H, 2H), 6.84 (d, J = 6.9 Hz, aryl H, 2H), 6.93 (d, J = 6.9 Hz, aryl H, 2H), 7.02 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 7.2 Hz, 2H), 9.60 (d, J = 3.3 Hz, aryl H, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ -0.23 ($SiMe_3$), 31.23 ($CSiMe_3$), 121.26, 121.94, 125.64, 129.09, 130.51, 138.55, 146.17, 148.09, 148.23 (C_9H_6N). ^{119}Sn NMR (C_6D_6, 149.2 MHz, $SnMe_4$ (ext.)): δ 5.38 (s).

Synthesis of $[\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Sn\rightarrow(\mu\text{-}CuCl)]_2$ (95) $[(R^2)_2Sn\rightarrow CuCl]_2$

To a stirring suspension of solid CuCl (0.14 g, 1.40mmol) in diethyl ether (20 mL) was added dropwise with a solution of $[Sn(R^2)_2]$ (**27**) (0.76 g, 1.40 mmol) in ether (25 mL) at 0 °C and raised to ambient temperature. The resultant yellow solution was stirred for 16 h. Black solid was formed and filtered off, the yellow filtrate was concentrated and stored at -30°C. Yellow crystals of **95** yielded 0.30g (14%). m.p. 213-215 °C (dec.). EI-MS: *m/z* 199 $[R^2]^+$. ^1H NMR (C_6D_6, 300.13 MHz): δ 0.10 (s, $SiMe_3$, 18H), 1.40 (s, $^2J(^{119}Sn, ^1H)$ = 60 Hz, CHSi, 2H), 6.64 (dd, J = 8.1 Hz, 3.9 Hz, aryl H, 2H), 6.79 (d, J = 5.7 Hz, aryl H, 2H), 6.90 (d, J = 8.1 Hz, aryl H, 2H), 6.98 (m, aryl H, 2H), 7.42 (d, J = 8.1 Hz, aryl H, 2H), 9.27 (br, aryl H, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ -1.16 ($SiMe_3$), 22.19 ($CSiMe_3$), 120.83, 121.20, 121.87, 124.18, 126.40, 130.52, 135.90, 147.78, 148.83. (C_9H_6N).

Synthesis of $[\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Sn\rightarrow(\mu\text{-}CuI)]_2$ (96) $[(R^2)_2Sn\rightarrow CuI]_2$

To a stirring solution of powdered CuI (0.20 g, 1.04 mmol) in diethyl ether (20 mL) was added dropwise with a solution of $[Sn(R^2)_2]$ (**27**) (0.57 g, 1.04 mmol) in ether (25 mL) at 0 °C and raised to ambient temperature. The resultant orange solution was stirred for 16 h. Grey solid was formed and filtered off, the orange filtrate was concentrated and stored at -30 °C. Orange crystals of **96** yielded 0.43 g (56%). m.p. 214-216 °C (dec.). Anal. Found: C, 44.27; H, 4.22; N, 3.85%. Calcd. for

$C_{26}H_{32}N_2Si_2SnCuI$: C, 42.32; H, 4.37; N, 3.79%. EI-MS: m/z 199 $[R^2]^+$. ^1H NMR (C_6D_6, 300.13 MHz): δ 0.16 (s, $SiMe_3$, 18H), 1.36 (s, $^2J(^{119}Sn, ^1H)$ = 14.1 Hz, CHSi, 2H), 6.67 (dd, J = 4.5 Hz, 13.9 Hz, aryl H, 2H), 6.81 (d, J = 6.3 Hz, aryl H, 2H), 6.97 (m, aryl H, 2H), 6.98 (m, aryl H, 4H), 7.42 (dd, J = 8.4 Hz, 7.2 Hz, aryl H, 2H), 9.72 (dd, J = 5.0 Hz, 3.3 Hz, aryl H, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ -0.04 ($SiMe_3$), 30.98 ($CSiMe_3$), 121.11, 121.84, 125.64, 129.15, 130.38, 138.45, 146.43, 148.16, 148.74 (C_9H_6N). ^{119}Sn NMR (C_6D_6, 149.2 MHz, $SnMe_4$ (ext.)): δ -90.27 (s).

APPENDIX II

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APPENDIX III

A. General procedures

All experiments were performed under a nitrogen atmosphere using standard Schelenk techniques, or in a M-BRAUN MB 150 M drybox. Solvents were dried over and freshly distilled, under nitrogen, from CaH_2 (hexane), and sodium benzophenone ketyl (THF, ether), sodium/potassium alloy (pentane, toluene), and degassed twice by freeze-thaw cycle prior to use.

B. Physical and analytical measurements

(i) Spectroscopic measurements:

^1H NMR spectra were recorded at 300.13 MHz using Bruker WM-300 spectrometer. Chemical shifts were referenced to residual solvent protons of δ 7.15 for C_6D_6, δ 7.24 for $CDCl_3$ and δ 7.00 for benzylic protons of C_7D_8.

$^{13}C\{^1H\}$ NMR spectra were recorded at 75.49 MHz using a Bruker WM-300 spectrometer. Chemical shifts were referenced to solvent peaks of δ 128.00 for C_6D_6 and δ 120.00 for benzylic carbon of C_7D_8.

^{119}Sn NMR spectra were recorded using a 400 MHz Varian NMR spectrometer at 149.20 MHz and chemical shifts were referenced externally to $SnMe_4$ at δ 0.00 ppm, respectively.

(ii) Microanalysis:

Elemental (C, H, N) analyses were performed by MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, Middlesex, U. K.

(iii) Melting point measurements:

Melting points were recorded on an Electrothermal Melting Point Apparatus and were uncorrected.

APPENDIX IV

Table A.1. Selected crystallographic data for compounds 29, 30,31

	29	**30**	**31**
Molecular formula	$C_{38}H_{54}Si_4N_4Ge$	$C_{38}H_{54}Si_4N_4Sn$	$C_{38}H_{54}Si_4N_4SnCl_2$
Molecular weight	751.80	797.90	1430.60
Color and habit	Orange prism	Yellow prism	Yellow prism
Crystal size, mm	0.30 x 0.25 x 0.24	0.24 x 0.22 x 0.18	0.30 x 0.22 x 0.20
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	Cc
a, Å	15.233(3)	11.986(2)	20.690(4)
b, Å	17.245(3)	12.005(2)	9.132(2)
c, Å	17.625(4)	17.091(3)	25.246(5)
α, deg	90	73.89(3)	90
β, deg	111.76(3)	85.94(3)	105.68(3)
γ, deg	90	63.27(3)	90
V, Å^3	4300.1(15)	2106.2(7)	4593(2)
Z	4	2	4
Density, g cm^{-3}	1.161	1.258	2.069
Abs. coeffs, mm^{-1}	0.853	0.750	1.346
Transmission factors	1.125-0.931	1.000-0.863	1.127-0.842
θ range for data collection	1.44-25.58°	2.02-26°	2.5-25.53°
Unique data measd.	6811	6770	5115
No. of variable, *p*	433	425	443
R	0.0567	0.0616	0.0512
wR	0.1420	0.1688	0.148

Table A. 2. Selected crystallographic data for compounds 59, 60, 61

	59	60	61
Molecular formula	$C_{38}H_{54}Si_4N_4GeS$	$C_{38}H_{54}Si_4N_4GeSe$	$C_{38}H_{54}Si_4N_4SnS$
Molecular weight	783.86	832.78	921.96
Color and habit	Yellow prism	Yellow prism	Yellow prism
Crystal size, mm	0.48 x 0.46 x 0.38	0.30 x 0.21 x 0.13	0.42 x 0.38 x 0.35
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a Å	11.290(2)	11.380(2)	12.136(2)
b, Å	12.724(3)	12.722(3)	10.975(2)
c, Å	15.977(3)	16.049(3)	36.470(7)
α, deg	77.49(3)	77.12(3)	
β, deg	89.89(3)	89.53(3)	92.34(3)
γ, deg	72.51(3)	72.42(3)	
V, Å^3	2132.1(7)	2154.9(7)	4853.5(17)
Z	2	2	4
Density, g cm^{-3}	1.221	1.283	1.233
Abs. coeffs, mm^{-1}	0.910	1.697	0.807
Transmission factors	1.000-0.879	1.455-0.484	
θ range for data collection	2.13-24.99°	1.73-25.00°	1.75-25.53°
Unique data measd.	7488	4741	6112
No. of variable, *p*	434	447	498
R	0.0496	0.0771	0.0711
wR	0.1366	0.1983	0.2022

Table A. 3. Selected crystallographic data for compounds 62, 91, 97

	62	91	97
Molecular formula	$C_{38}H_{54}Si_4N_4SnSe$	$C_{26}H_{32}N_2Si_2SnAgCl$	$C_{28}H_{32}N_4Si_2SnO_2$
Molecular weight	876.86	691.5	631
Color and habit	Yellow prism	Yellow prism	Colorless prism
Crystal size, mm	0.24 x 0.20 x 0.18	0.22 x 0.22 x 0.20	0.40 x 0.36 x 0.36
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	P2/c
a Å	11.395(2)	12.250(3)	14.442(3)
b, Å	12.778(3)	14.586(3)	10.723(2)
c, Å	16.129(3)	16.891(3)	20.068(4)
α, deg	78.78(3)	90	90
β, deg	89.01(3)	97.00(3)	97.86(3)
γ, deg	72.99(3)	90	90
V, Å^3	2200.8(8)	2995.6(10)	3078.6(11)
Z	2	2	2
Density, g cm^{-3}	1.323	1.172	1.362
Abs. coeffs, mm^{-1}	1.546	1.652	0.937
Transmission factors	1.164-0.742	1.169-0.939	1.138-0.964
θ range for data collection	1.87-25.6°	1.85-25.59°	
Unique data measd.	5560	4259	5003
No. of variable, *p*	475	341	354
R	0.0627	0.0645	0.0421
wR	0.1775	0.1654	0.1176